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| Title        | Studies on Low-Temperature Operative Catalytic Combustion-Type Methane Gas Sensors Employing Novel Catalysts with Apatite-Type Rare Earth Silicate Promoters |
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The University of Osaka

Doctoral Dissertation

**Studies on Low-Temperature Operative Catalytic Combustion-  
Type Methane Gas Sensors Employing Novel Catalysts with  
Apatite-Type Rare Earth Silicate Promoters**

(アパタイト型希土類ケイ酸塩を助触媒として  
用いた低温作動型接触燃焼式メタンガスセンサに関する研究)

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January 2026

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## *Preface*

The study of this doctoral thesis has been conducted under the direct supervision of Professor Dr. Nobuhito Imanaka, Associate Professor Dr. Shinji Tamura, and Professor Dr. Daisuke Kan in the division of Applied Chemistry, Graduate School of Engineering, The University of Osaka.

The objective of this thesis is to develop catalytic combustion-type methane gas sensors capable of low-temperature operation.

The author hopes that the findings and knowledge obtained in this study will contribute to the further design and development of low-temperature operative catalytic combustion-type methane gas sensors for more practical applications.

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January 2026

## ***Contents***

|                                    |       |   |
|------------------------------------|-------|---|
| <b><i>General Introduction</i></b> | ..... | 1 |
|------------------------------------|-------|---|

### ***Chapter 1***

#### **Low-Temperature Operative Catalytic Combustion-Type Methane Gas Sensors Employing Apatite-type $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$ -Supported Palladium Oxide**

|     |                        |       |    |
|-----|------------------------|-------|----|
| 1.1 | Introduction           | ..... | 6  |
| 1.2 | Experimental Procedure | ..... | 6  |
| 1.3 | Results and Discussion | ..... | 9  |
| 1.4 | Conclusion             | ..... | 17 |

### ***Chapter 2***

#### **Effects of Apatite-Type Lanthanoid Silicate Promoters on Catalytic Activity and Methane Sensing Performance of $\text{PdO}/\text{Ln}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$ Sensors**

|     |                        |       |    |
|-----|------------------------|-------|----|
| 2.1 | Introduction           | ..... | 18 |
| 2.2 | Experimental Procedure | ..... | 18 |
| 2.3 | Results and Discussion | ..... | 19 |
| 2.4 | Conclusion             | ..... | 30 |

## ***Chapter 3***

### **Catalytic Combustion-Type Methane Gas Sensor with Tungsten-Doped Apatite-Type Gadolinium Silicate**

|                                        |                        |       |          |
|----------------------------------------|------------------------|-------|----------|
| 3.1                                    | Introduction           | ..... | 31       |
| 3.2                                    | Experimental Procedure | ..... | 32       |
| 3.3                                    | Results and Discussion | ..... | 32       |
| 3.4                                    | Conclusion             | ..... | 39       |
| <br><b><i>Summary</i></b>              |                        |       | ..... 40 |
| <br><b><i>References</i></b>           |                        |       | ..... 43 |
| <br><b><i>List of Publications</i></b> |                        |       | ..... 46 |
| <br><b><i>Acknowledgements</i></b>     |                        |       | ..... 47 |

## ***General Introduction***

Natural gas is extensively used as an energy source for power generation, residential fuel supply, and transportation. Owing to its lower carbon dioxide ( $\text{CO}_2$ ) emissions and the absence of sulfur oxides ( $\text{SO}_x$ ) compared with coal and petroleum, natural gas is regarded as a relatively clean fossil fuel, and its global demand continues to rise. However, methane ( $\text{CH}_4$ ), the primary component of natural gas, possesses a global warming potential approximately 25 times greater than that of  $\text{CO}_2$  on a mass basis, making it one of the most potent greenhouse gases [1, 2]. Unintentional leakage of  $\text{CH}_4$  into the atmosphere significantly accelerates global warming and deteriorates the environment. Therefore, continuous, quantitative, and real-time monitoring of atmospheric  $\text{CH}_4$  concentrations is essential for ensuring environmental safety and mitigating climate change.

Several types of  $\text{CH}_4$  gas sensors are used for real-time monitoring, including semiconductor-type [3–5], electrochemical-type [6–8], and catalytic combustion-type sensors [9–12]. Each sensor type offers characteristic advantages but also presents inherent limitations. Semiconductor gas sensors detect low concentrations of target gases through changes in electrical resistance induced by gas adsorption on the semiconductor surface. Their high sensitivity and compatibility with miniaturized, low-power devices have led to widespread residential use. However, adsorption site saturation causes signal plateauing at high gas concentrations, preventing quantitative detection. Furthermore, surface adsorption-based sensing inherently suffers from low gas selectivity, limiting applicability in complex environments. Electrochemical sensors function through redox reactions between the target gas and a liquid electrolyte at the electrode interface. Because each gas reacts at a distinct electrochemical potential, these sensors offer excellent selectivity and sensitivity under controlled conditions, making them valuable for industrial measurements. Nevertheless, the evaporation and leakage of liquid electrolytes restrict operational lifetime and long-term stability.

In contrast, catalytic combustion-type gas sensors possess a simple structure consisting of a

Pt coil coated with a CH<sub>4</sub> oxidation catalyst. These sensors offer advantages such as high durability, ease of fabrication, and suitability for mass production. The sensing mechanism is based on the exothermic oxidation of combustible gases on the catalyst surface; the resulting combustion heat increases the temperature of the embedded Pt coil, which in turn changes its electrical resistance. This resistance change serves as the sensor output and is proportional to CH<sub>4</sub> concentration. Owing to their excellent quantitative performance, long lifetime, and sensitivity, catalytic combustion-type sensors are widely used in safety management and explosion-prevention applications.

However, CH<sub>4</sub> is the most thermodynamically stable combustible gas due to its four strong C–H covalent bonds (approximately 413 kJ·mol<sup>-1</sup>) and tetrahedral molecular structure, requiring temperatures above 1000 °C for thermal decomposition under non-catalytic conditions [13, 14]. Even when employing oxidation catalysts composed of PdO (high CH<sub>4</sub> oxidation activity) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (high surface area), complete CH<sub>4</sub> oxidation still requires temperatures exceeding 450 °C [15, 16]. At these elevated temperatures, other combustible gases such as CO and H<sub>2</sub> are also oxidized, making it difficult for a single catalytic combustion sensor element to maintain high selectivity toward CH<sub>4</sub>. A common strategy to address this challenge is the combined use of multiple sensors with different gas-dependent operating temperatures to enhance selectivity. Simultaneously, developing catalysts capable of promoting CH<sub>4</sub> oxidation at lower temperatures can reduce cross-sensitivity and minimize the number of required sensing elements. Lower operating temperatures also reduce power consumption, contributing to improved energy efficiency.

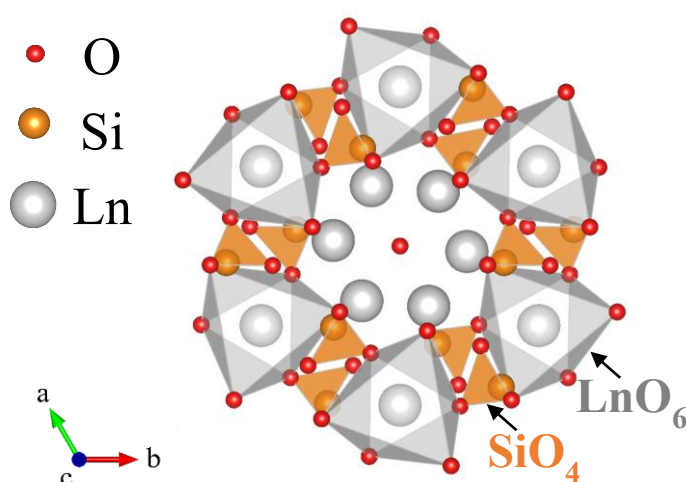
One promising approach to facilitating CH<sub>4</sub> combustion at lower temperatures is the supply of highly reactive oxygen species (e.g., atomic oxygen, oxygen radicals, ionic oxygen species) to the primary catalyst instead of relying solely on atmospheric molecular oxygen. By enabling low-temperature CH<sub>4</sub> oxidation, such promoters are expected to improve CH<sub>4</sub> detection performance at reduced sensor temperatures. Previous studies have investigated various promoters capable of supplying reactive oxygen species to the primary catalyst, as summarized in Table G-1 [17-19]. In CH<sub>4</sub> combustion catalysts, materials such as CeO<sub>2</sub>-ZrO<sub>2</sub>, LaFeO<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub> function as promoters that

**Table G-1.** Research trends of reactive oxygen species supply promoters for CH<sub>4</sub> oxidation.

| Promoter                                   | Reactive oxygen species supply mechanism                      | Characteristics                       | Ref. |
|--------------------------------------------|---------------------------------------------------------------|---------------------------------------|------|
| CeO <sub>2</sub> -ZrO <sub>2</sub>         | Ce <sup>4+</sup> / Ce <sup>3+</sup> redox with V <sub>O</sub> | High OSC<br>(Oxygen Storage Capacity) | [17] |
| LaFeO <sub>3</sub><br>(Perovskite)         | Oxygen vacancy migration                                      | Enhanced lattice oxygen mobility      | [18] |
| Co <sub>3</sub> O <sub>4</sub><br>(Spinel) | Lattice oxygen supply                                         | Strong interaction with Pd (SMSI)     | [19] |

provide reactive oxygen species and are subsequently reoxidized by gas-phase O<sub>2</sub> under lean conditions. Although their oxygen-supply mechanisms differ, each promoter effectively facilitates CH<sub>4</sub> oxidation at lower temperatures. Nevertheless, these promoters have mainly been utilized to improve CH<sub>4</sub> combustion at relatively high temperatures, and further reduction of the operating temperature remains necessary for the objectives of this study.

In this research, apatite-type rare-earth silicates (Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>; Ln = rare-earth element), which exhibit oxide-ion mobility even at relatively low temperatures (ca. 300–500 °C), were selected as promoters to develop catalytic combustion-type CH<sub>4</sub> gas sensors operable at low temperature [20–22]. The apatite-type structure contains abundant oxygen defects and one-dimensional *c*-axis channels formed by LnO<sub>6</sub> and SiO<sub>4</sub> units (Figure G-1), which enable oxide-ion migration [23]. These structural features enhance the supply of reactive oxygen species and thereby improve CH<sub>4</sub> oxidation catalysis even at low temperatures [24]. However, systematic investigations of the low-temperature CH<sub>4</sub> sensing characteristics of catalysts incorporating apatite-type promoters, as well as the effects of promoter properties and optimal promoter compositions for sensor applications, have not yet been conducted. Accordingly, this dissertation elucidates the influences of apatite-type promoters and their compositions on catalytic activity and CH<sub>4</sub> sensing performance in catalytic combustion-type gas sensors.



**Figure G-1.** Crystal structure of apatite-type  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}$ .

Importantly, enhanced catalytic activity alone does not necessarily translate into improved sensor performance. Achieving high catalytic activity generally requires a large specific surface area and numerous oxygen defects, which increase active sites and reactive oxygen species supply. However, these characteristics simultaneously impede heat transfer within the catalyst, reducing thermal conductivity and increasing specific heat capacity by increasing lattice vibrational degrees of freedom. Since the thermal transport properties of the material are governed by both thermal conductivity and specific heat capacity, high thermal conductivity promotes efficient heat transfer from the catalyst surface to the Pt coil, whereas low specific heat capacity results in a greater temperature rise for a given amount of combustion heat. If the thermal transport properties of the catalyst are insufficient, the combustion heat generated on its surface cannot be efficiently transferred to the Pt coil, leading to reduced sensitivity (sensor output per  $\text{CH}_4$  concentration) and slower response. Therefore, high-performance catalytic combustion-type  $\text{CH}_4$  gas sensors require a balanced optimization of catalytic and thermal transport properties; improving either property alone is inadequate.

In the laboratory to which the author belongs, the thermal transport properties of catalytic combustion-type sensors have previously been improved using two strategies: accelerating sensor response by coating the Pt coil with aluminum nitride (AlN), a high-thermal-conductivity material [25], and enhancing sensitivity by mixing artificial diamond with superior thermal conductivity into the catalyst [26]. These strategies, however, primarily focus on enhancing thermal conductivity to facilitate heat transfer from the combustion region to the Pt coil. As discussed above, the specific heat capacity of the catalyst is also a key factor; reducing specific heat capacity increases the temperature rise per unit combustion heat, directly contributing to higher sensitivity and faster sensor response. Despite its importance, reducing catalyst specific heat capacity to improve thermal transport in catalytic combustion-type CH<sub>4</sub> sensors has rarely been explored. Therefore, this dissertation first clarifies how apatite-type promoters and their compositions influence low-temperature CH<sub>4</sub> catalytic activity and subsequently investigates the specific heat capacity of the catalyst as a key parameter governing low-temperature sensitivity and response characteristics of catalytic combustion-type CH<sub>4</sub> gas sensors.

This thesis consists of the following three chapters.

In **Chapter 1**, gadolinium silicate—reported to exhibit superior thermal and chemical stability among rare-earth silicates—was selected as a promoter for PdO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts to achieve low-temperature CH<sub>4</sub> oxidation, and the catalytic activity and CH<sub>4</sub> sensing performance of PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were evaluated.

In **Chapter 2**, to elucidate the effects of promoter composition on catalyst properties and CH<sub>4</sub> sensing characteristics, PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts were synthesized and evaluated.

In **Chapter 3**, to improve low-temperature sensitivity by reducing specific heat capacity through W<sup>6+</sup> doping at Si<sup>4+</sup> sites in Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>, PdO/Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+8</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0 ≤ x ≤ 1.0) catalysts were synthesized and evaluated.

## **Chapter 1**

# **Low-Temperature Operative Catalytic Combustion-Type Methane Gas Sensors Employing Apatite-type $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$ -Supported Palladium Oxide**

## **1.1. Introduction**

As described in the General Introduction, high-performance catalytic combustion-type gas sensors require an appropriate balance between catalytic activity and thermal stability. Therefore, promoters capable of supplying reactive oxygen species to PdO and facilitating  $\text{CH}_4$  combustion at low temperatures were first examined. Among various promoter candidates, apatite-type lanthanoid silicates are known to exhibit excellent oxide-ion mobility even at low temperatures, thereby enhancing  $\text{CH}_4$  combustion and  $\text{CH}_4$  sensing performance.

In this chapter,  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  was selected as the promoter among apatite-type lanthanoid silicates because it is expected to withstand the harsh operating conditions of catalytic combustion-type gas sensors, including high temperatures, frequent temperature fluctuations, and repeated redox cycles. Gadolinium silicate exhibits superior thermal and chemical stability compared with other lanthanoid silicates [27, 28]. Accordingly, a  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalyst was synthesized by combining the  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  promoter with PdO as the primary catalyst and  $\gamma\text{-Al}_2\text{O}_3$  as the support, and its catalytic activity and  $\text{CH}_4$  sensing performance were evaluated.

## **1.2. Experimental Procedure**

An  $x$  wt.% PdO/( $1-x$ ) wt.%  $\{y$  wt.%  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/(100-y)$  wt.%  $\gamma\text{-Al}_2\text{O}_3\}$  catalyst ( $0 \leq x \leq 17$ ,  $0 \leq y \leq 30$ ) was synthesized according to the following procedure. For convenience, these catalysts are hereafter denoted as  $x$  wt.% PdO/ $y$  wt.%  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$ .

$\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  was prepared by the sol-gel method. A stoichiometric mixture of  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Shin-Etsu Chemical Co., Ltd.) and  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (Kishida Chemical) was dissolved in deionized water

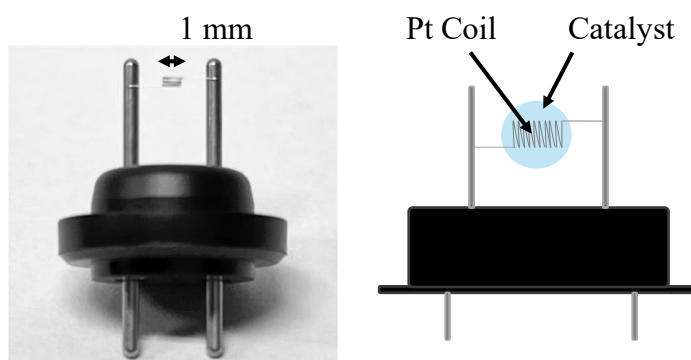
to form a sol, and acetic acid was added to adjust the pH, resulting in gel formation under continuous stirring. After stirring for 1 h at 25 °C, the wet gel was heated at 180 °C for 1 h and subsequently calcined at 350 °C for 4 h in air. The resulting powder was further calcined at 1000 °C for 2 h in air.

Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> was supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by weighing the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> powder so that its content became  $y$  wt.% relative to the total amount of Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> +  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $0 \leq y \leq 30$ ). The mixed powders were wet-mixed in ethanol using a ball mill (Pulverisette 7, FRITSCH) and then heated in air at 500 °C for 4 h. PdO was loaded by an impregnation method. The synthesized  $y$  wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated with a Pd(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> solution (Tanaka Kikinzoku Kogyo) so that the Pd content became  $x$  wt.% ( $0 \leq x \leq 17$ ). The suspension was stirred at room temperature for 6 h, the solvent was removed at 180 °C, and the sample was calcined at 500 °C for 4 h in a flow of synthetic air to obtain  $x$  wt.% PdO/ $y$  wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Sample characterization was performed by X-ray fluorescence (XRF; Supermini200, Rigaku) analysis and X-ray powder diffraction (XRD; SmartLab, Rigaku) using Cu K $\alpha$  radiation (40 kV, 30 mA) in the  $2\theta$  range from 10° to 70°. Specific surface areas were obtained from nitrogen adsorption–desorption isotherms measured at –196 °C by the Brunauer–Emmett–Teller (BET) method (Tristar 3000, Shimadzu). The stability of the catalyst under a reducing atmosphere was evaluated by temperature-programmed reduction (TPR) under 5 vol.% H<sub>2</sub>/Ar at a flow rate of 50 mL·min<sup>–1</sup> and a heating rate of 5 °C·min<sup>–1</sup> (BELCAT-B, MicrotracBEL). CH<sub>4</sub> oxidation activity was measured using a fixed-bed reactor consisting of a quartz tube with an inner diameter of 10 mm. The feed gas was composed of 1 vol.% CH<sub>4</sub> in air at a flow rate of 33.4 mL·min<sup>–1</sup> (space velocity: 20,000 L·kg<sup>–1</sup>·h<sup>–1</sup>).

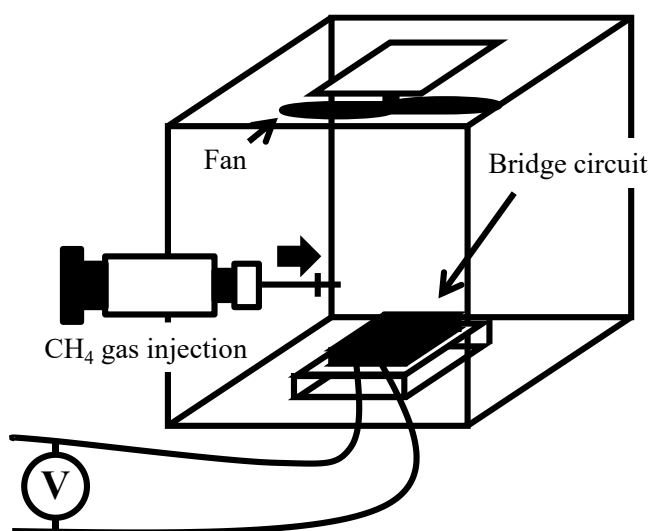
Figure 1.1 illustrates the CH<sub>4</sub> gas sensor element fabricated with the catalyst. The sensor element was fabricated using a Pt coil with a length of 1 mm, made from a Pt wire with a diameter of 30  $\mu$ m. The catalyst was dispersed in glycerin to form a slurry, and the Pt coil was coated with this slurry. The coated Pt coil was subsequently heated to approximately 300 °C for 10 min to evaporate the glycerin and sinter the catalyst on the coil.

The sensor element was incorporated into a measurement bridge circuit, and sensor tests were



**Figure 1.1** Schematic illustration of the established sensor element.

conducted in a chamber with a volume of  $5.3 \times 10^{-2} \text{ m}^3$ , as shown in Figure 1.2. After placing the sensor element in the chamber, it was heated by applying a DC voltage to the Pt coil until the desired operating temperature was reached. The  $\text{CH}_4$  concentration (0–1000 ppm) in the chamber was controlled by introducing appropriate amounts of 99.9%  $\text{CH}_4$  using a syringe. The sensor signal in response to  $\text{CH}_4$  exposure was defined as  $(V_{\text{gas}} - V_{\text{air}})$ , where  $V_{\text{gas}}$  and  $V_{\text{air}}$  are the sensor voltages measured in the test gas containing  $\text{CH}_4$  and in pure air, respectively. The coefficient of determination ( $R^2$ ), representing the linearity between sensor signal and  $\text{CH}_4$  concentration, was evaluated. In this study, quantitative  $\text{CH}_4$  detection was defined as an  $R^2$  value greater than 0.990. The sensor response



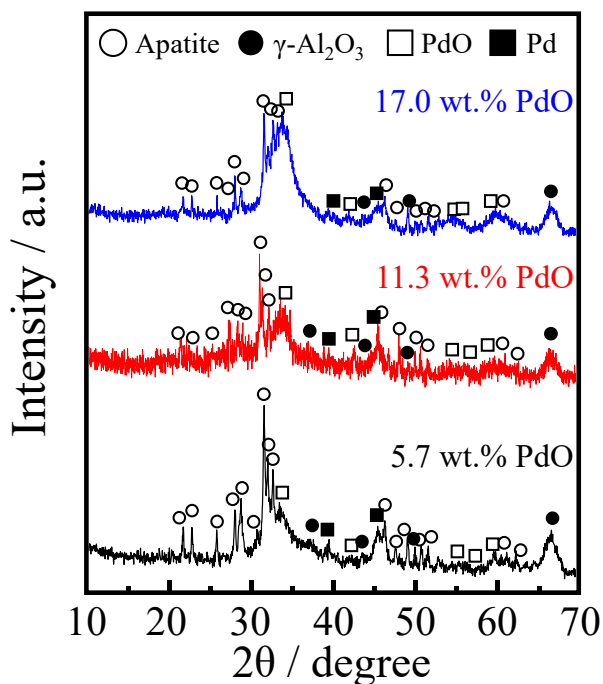
**Figure 1.2** Schematic diagram of the sensor measurement system.

time,  $T_{50}$ , was defined as the time required for the sensor voltage to reach 50% of its equilibrium value at a given  $\text{CH}_4$  concentration.

### 1.3. Results and Discussion

First, the loading amounts of the primary catalyst PdO, the promoter, and the  $\gamma\text{-Al}_2\text{O}_3$  support were optimized with respect to  $\text{CH}_4$  sensing performance. The crystalline phases and catalyst loadings were confirmed by XRD and XRF, and the sensing characteristics of the fabricated sensors were subsequently evaluated.

The XRD patterns of  $x$  wt.% PdO/20 wt.%  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  ( $5.7 \leq x \leq 17$ ) catalysts are shown in Figure 1.3. For all samples, only diffraction peaks corresponding to apatite-type silicate, PdO, Pd, and  $\gamma\text{-Al}_2\text{O}_3$  were observed, confirming that the catalysts are phase-pure and free from secondary phases. Furthermore, the intensity of the PdO (101) peak at approximately  $33.8^\circ$  increased with increasing PdO loading. The measured compositions of the catalysts, listed in Table 1.1, agree well with the nominal stoichiometric values within experimental error.

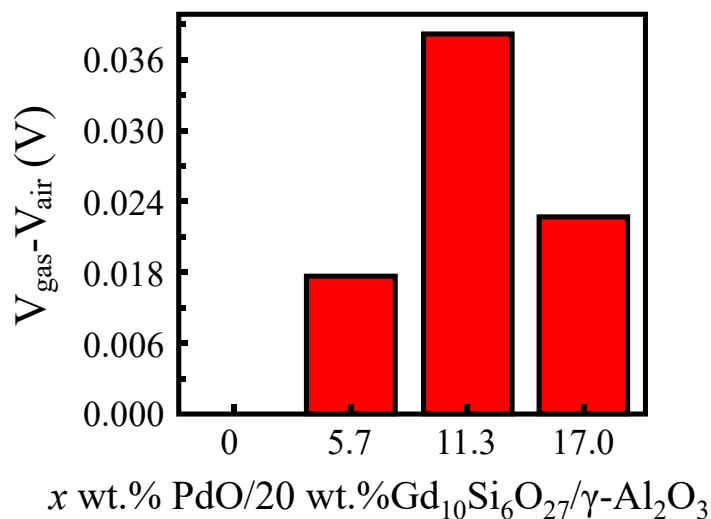


**Figure 1.3** XRD patterns of the (5.7–17) wt.% PdO/20 wt.%  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalysts.

**Table 1.1** Measured compositions of the  $x$  wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $5.7 \leq x \leq 17$ ) catalysts.

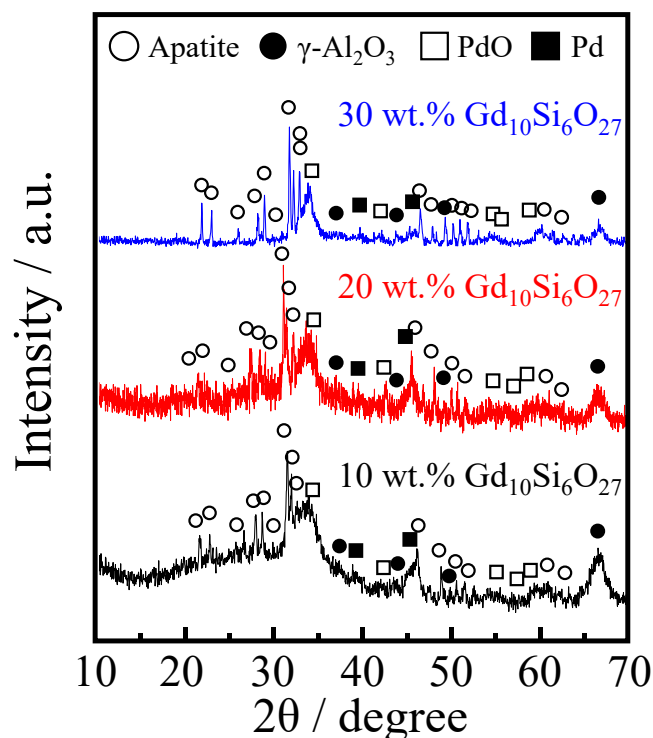
| Catalyst                                                                                                    | Measured composition                                                                                          |
|-------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| 17.0 wt.% PdO/20 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 16.5 wt.% PdO/18.5 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> |
| 11.3 wt.% PdO/20 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 13.9 wt.% PdO/18.5 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> |
| 5.7 wt.% PdO/20 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub>  | 5.9 wt.% PdO/18.5 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub>  |

Figure 1.4 shows the sensor output values for 1000 ppm CH<sub>4</sub> at 375 °C using  $x$  wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $0 \leq x \leq 17$ ). The sensor employing the catalyst with a PdO content of 11.3 wt.% exhibited the highest output. This trend suggests that the number of active PdO sites is insufficient at lower PdO loadings, whereas PdO aggregation may occur at higher loadings, leading to reduced catalytic activity. In the absence of PdO (0 wt.%), no measurable response to CH<sub>4</sub> was observed, indicating that PdO is essential for CH<sub>4</sub> sensing. Accordingly, the optimal PdO loading was determined to be 11.3 wt.%.



**Figure 1.4** Sensor output value for 1000 ppm CH<sub>4</sub> at 375 °C for the sensors using  $x$  wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $0 \leq x \leq 17$ ) catalysts.

The CH<sub>4</sub> sensing performance was also investigated as a function of promoter loading. The XRD patterns of 11.3 wt.% PdO/*y* wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (10 ≤ *y* ≤ 30) catalysts are shown in Figure 1.5. For all samples, only diffraction peaks assigned to apatite-type silicate, PdO, Pd, and γ-Al<sub>2</sub>O<sub>3</sub> were observed. As the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> loading increased, the relative amount of γ-Al<sub>2</sub>O<sub>3</sub> decreased, resulting in a reduction in the intensity of the γ-Al<sub>2</sub>O<sub>3</sub> (440) peak at approximately 66.8°. The measured



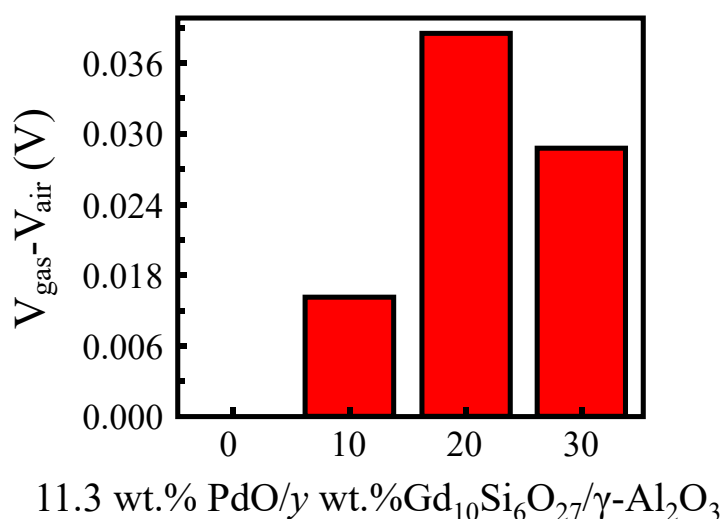
**Figure 1.5** XRD patterns of the 11.3 wt.% PdO/*y* wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (10 ≤ *y* ≤ 30) catalysts.

**Table 1.2** Measured compositions of the 11.3 wt.% PdO/*y* wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (10 ≤ *y* ≤ 30) catalysts.

| Catalyst                                                                                                    | Measured composition                                                                                          |
|-------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| 11.3 wt.% PdO/30 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 13.9 wt.% PdO/28.6 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> |
| 11.3 wt.% PdO/20 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 13.9 wt.% PdO/18.5 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> |
| 11.3 wt.% PdO/10 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 13.9 wt.% PdO/11.6 wt.%<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> |

compositions listed in Table 1.2 are consistent with the nominal values within experimental error.

Figure 1.6 shows the sensor output values for 1000 ppm CH<sub>4</sub> at 375 °C using 11.3 wt.% PdO/*y* wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (10 ≤ *y* ≤ 30). The highest output was obtained for the sensor containing 20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>. At lower promoter loadings, the amount of Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> is presumably insufficient to effectively assist oxygen supply to PdO active sites, whereas at higher loadings the reduced γ-Al<sub>2</sub>O<sub>3</sub> content may adversely affect catalyst dispersion. In the absence of the promoter (0 wt.%), no response was observed at 375 °C; however, a detectable signal appeared at operating temperatures above 435 °C (Figure 1.9). Therefore, the optimal Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> loading was determined to be 20 wt.% under the present conditions.



**Figure 1.6** Sensor output value for 1000 ppm CH<sub>4</sub> at 375 °C for the sensors using 11.3 wt.% PdO/*y* wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (10 ≤ *y* ≤ 30) catalysts.

Based on these optimization results, 11.3 wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was identified as the optimal composition for low-temperature CH<sub>4</sub> sensing. Hereafter, this compositional catalyst is denoted as PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.

Table 1.3 lists the BET surface areas of Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>, γ-Al<sub>2</sub>O<sub>3</sub>, Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, PdO/γ-Al<sub>2</sub>O<sub>3</sub>, and PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. Although the specific surface area of Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> was relatively

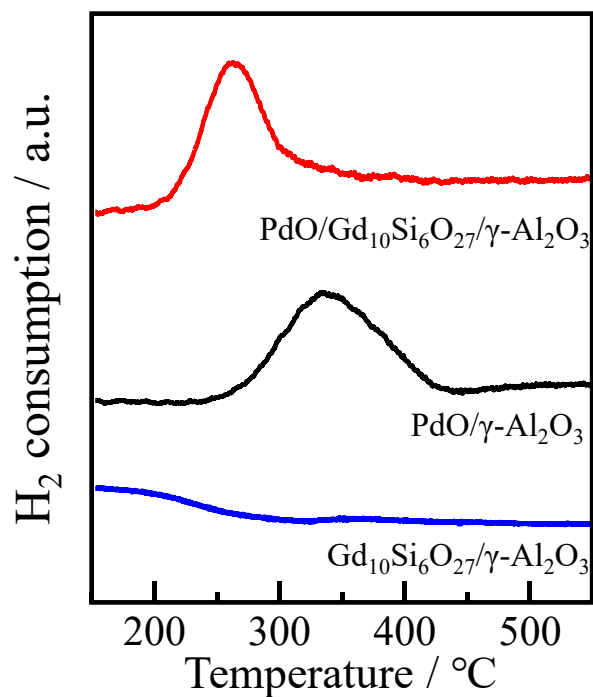
low ( $4.9 \text{ m}^2 \cdot \text{g}^{-1}$ ) due to high-temperature calcination, the  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalyst maintained a relatively high surface area of  $98.8 \text{ m}^2 \cdot \text{g}^{-1}$  owing to the presence of the  $\gamma\text{-Al}_2\text{O}_3$  support ( $191.0 \text{ m}^2 \cdot \text{g}^{-1}$ ).

**Table 1.3** BET surface area of  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$ ,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{PdO}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  samples.

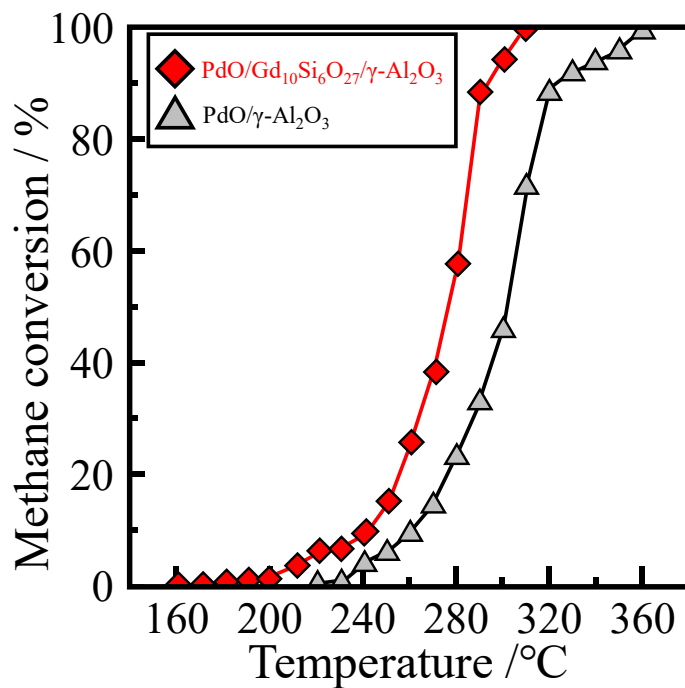
| Sample                                                                           | BET surface area / $\text{m}^2 \cdot \text{g}^{-1}$ |
|----------------------------------------------------------------------------------|-----------------------------------------------------|
| $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$                                         | 4.9                                                 |
| $\gamma\text{-Al}_2\text{O}_3$                                                   | 191.0                                               |
| $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$            | 115.5                                               |
| $\text{PdO}/\gamma\text{-Al}_2\text{O}_3$                                        | 148.9                                               |
| $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$ | 98.81                                               |

Figure 1.7 demonstrates the  $\text{H}_2$ -TPR profiles of  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{PdO}/\gamma\text{-Al}_2\text{O}_3$ , and  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$ . A reduction peak was observed for all samples.  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  exhibited a broad, low-intensity peak above  $100^\circ\text{C}$ , suggesting gradual oxygen release from the  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  promoter. Since  $\gamma\text{-Al}_2\text{O}_3$  alone showed no reduction peak, the peak observed around  $300^\circ\text{C}$  for the  $\text{PdO}$ -loaded samples is attributed to oxygen release from  $\text{PdO}$  [29]. The  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalyst exhibited a reduction peak at a lower temperature than  $\text{PdO}/\gamma\text{-Al}_2\text{O}_3$ , despite its lower total  $\text{H}_2$  consumption. This peak shift is attributed to an increased fraction of  $\text{Pd}^{2+}$  species induced by the promoter, leading to the formation of weakly bound  $\text{Pd}^{2+}\text{-O}$  species at the  $\text{PdO}\text{-Gd}_{10}\text{Si}_6\text{O}_{27}$  interface with enhanced reducibility [30, 31]. The decreased  $\text{H}_2$  consumption is attributed to the additional formation of strongly bound bulk  $\text{Pd}^{2+}\text{-O}$  species [32]. These results indicate that the  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  promoter enhances oxygen-release ability, supplying reactive oxygen species at lower temperatures and thereby improving low-temperature  $\text{CH}_4$  sensing performance.

Figure 1.8 shows the temperature dependence of  $\text{CH}_4$  combustion activity for  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{PdO}/\gamma\text{-Al}_2\text{O}_3$ . The  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalyst began converting  $\text{CH}_4$  above  $160^\circ\text{C}$  and achieved complete  $\text{CH}_4$  combustion at  $310^\circ\text{C}$ , demonstrating superior low-



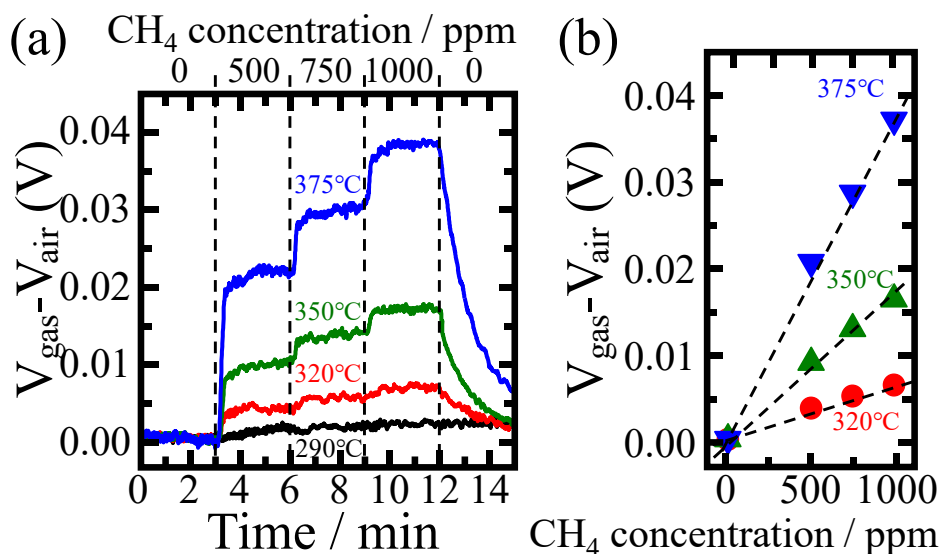
**Figure 1.7** H<sub>2</sub>-TPR profiles of the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/γ-Al<sub>2</sub>O<sub>3</sub> catalysts and the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> promoter.



**Figure 1.8** Temperature dependence of CH<sub>4</sub> conversion for the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/γ-Al<sub>2</sub>O<sub>3</sub> catalysts.

temperature activity compared with PdO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This enhancement is attributed to the high oxide-ion mobility of Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>, which increases the supply of reactive oxygen species to PdO.

Figure 1.9 shows the sensor response curves to stepwise changes in CH<sub>4</sub> concentration for the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sensor at temperatures above 290 °C and the sensor output as a function of CH<sub>4</sub> concentration at temperatures from 320 to 375 °C. The sensor performance parameters are summarized in Table 1.4. At 290 °C, the sensor output gradually increased with time and did not clearly follow changes in CH<sub>4</sub> concentration. In contrast, at temperatures above 320 °C, the sensor exhibited stepwise responses with T<sub>50</sub> values of 11–13 s. Moreover, a linear relationship between sensor output and CH<sub>4</sub> concentration was observed, with R<sup>2</sup> values exceeding 0.990, indicating quantitative CH<sub>4</sub> detection.

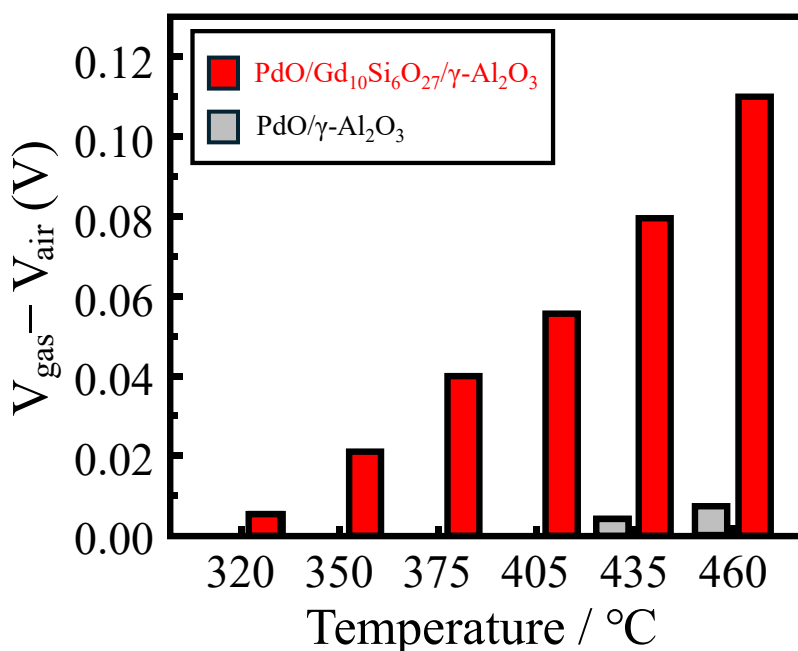


**Figure 1.9** (a) Response curves and (b) sensor outputs at various CH<sub>4</sub> concentrations for the sensor incorporating the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at various temperatures.

**Table 1.4** Sensing properties of sensors using the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst toward CH<sub>4</sub>.

| Temperature / °C | R <sup>2</sup> | T <sub>50</sub> / s | Sensor output for 1000 ppm CH <sub>4</sub> / V |
|------------------|----------------|---------------------|------------------------------------------------|
| 320              | 0.993          | 13                  | 0.0067                                         |
| 350              | 0.997          | 13                  | 0.0173                                         |
| 375              | 0.996          | 11                  | 0.0393                                         |

Figure 1.10 depicts the temperature dependence of sensor output for 1000 ppm CH<sub>4</sub> using PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/γ-Al<sub>2</sub>O<sub>3</sub> catalysts and Table 1.5 summarizes the sensor output values at 435 °C and the operating temperature at which each sensor provides a quantitative response to CH<sub>4</sub>. The sensor employing PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> achieved quantitative CH<sub>4</sub> detection at 320 °C, which is 115 °C lower than that required for the PdO/γ-Al<sub>2</sub>O<sub>3</sub> sensor (435 °C). Furthermore, the sensor output at 435 °C was more than 20 times higher than that of the sensor without the promoter. This enhancement is attributed to increased reactive oxygen supply from the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter, promoting CH<sub>4</sub> combustion at lower temperatures and generating greater combustion heat.

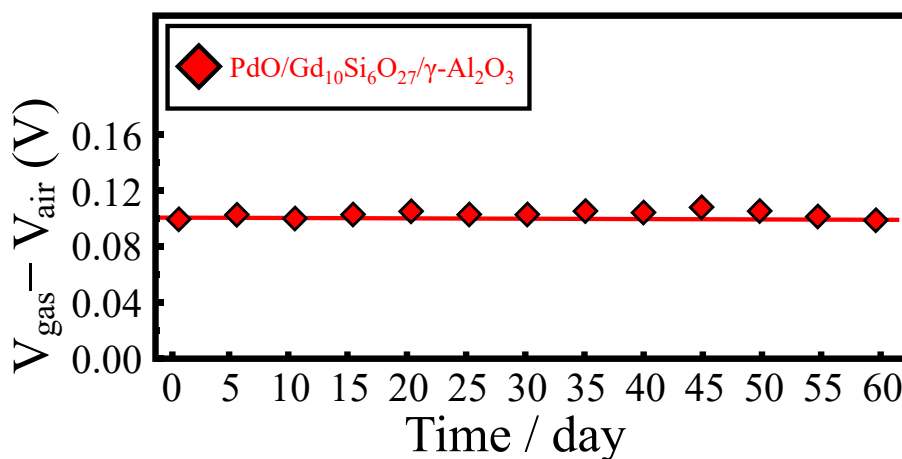


**Figure 1.10** Temperature dependence of output values for 1000 ppm CH<sub>4</sub> for sensors using PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO /γ-Al<sub>2</sub>O<sub>3</sub> catalysts.

**Table 1.5** Sensing output at 435 °C and operating temperature of the sensors using the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO /γ-Al<sub>2</sub>O<sub>3</sub> catalysts.

| Sensor                                                                                 | Sensor output for 1000 ppm CH <sub>4</sub> / V | Operating temperature / °C |
|----------------------------------------------------------------------------------------|------------------------------------------------|----------------------------|
| PdO/γ-Al <sub>2</sub> O <sub>3</sub>                                                   | 0.0037                                         | 435                        |
| PdO/Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 0.0792                                         | 320                        |

Figure 1.11 shows the long-term stability of the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> sensor under continuous exposure to 1000 ppm CH<sub>4</sub> at 460 °C. Stable sensor output was maintained for 60 days without noticeable degradation.



**Figure 1.11** Time dependence of output values for 1000 ppm CH<sub>4</sub> for sensor using PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> at 460 °C.

## 1.4. Conclusion

In this chapter, an 11.3 wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst employing apatite-type gadolinium silicate with high oxide-ion mobility and excellent thermal and chemical stability was synthesized and applied to a catalytic combustion-type CH<sub>4</sub> gas sensor. The Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter enhanced oxygen-release ability and CH<sub>4</sub> oxidation activity, enabling stable and quantitative CH<sub>4</sub> detection at temperatures of 320 °C and above.

## **Chapter 2**

# Effects of Apatite-Type Lanthanoid Silicate Promoters on Catalytic Activity and Methane Sensing Performance of PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Sensors

## **2.1. Introduction**

Chapter 1 demonstrated that a catalytic combustion-type CH<sub>4</sub> sensor employing 11.3 wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> could detect CH<sub>4</sub> quantitatively and stably at 320 °C, which is more than 115 °C lower than the operating temperature of a sensor without a promoter. This improvement in low-temperature CH<sub>4</sub> sensing performance was attributed to the use of apatite-type Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> as a promoter, which enhanced CH<sub>4</sub> combustion activity by facilitating the supply of oxygen species to PdO and thereby increasing combustion heat at low operating temperatures.

However, Chapter 1 focused on a single promoter composition and did not clarify which intrinsic properties of the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter govern the superior CH<sub>4</sub> sensing performance. Therefore, the present chapter aims to elucidate which physicochemical properties of apatite-type materials dominate catalytic activity and CH<sub>4</sub> sensing behavior. To this end, 11.3 wt.% PdO/20 wt.% Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts were synthesized, and key factors influencing catalytic combustion-type gas sensor performance—including specific heat capacity, specific surface area, catalytic activity, and oxygen release properties—were systematically evaluated. Catalytic combustion-type CH<sub>4</sub> sensors were then fabricated using these catalysts, and the relationships between these properties and sensor performance were comprehensively investigated.

## **2.2. Experimental Procedure**

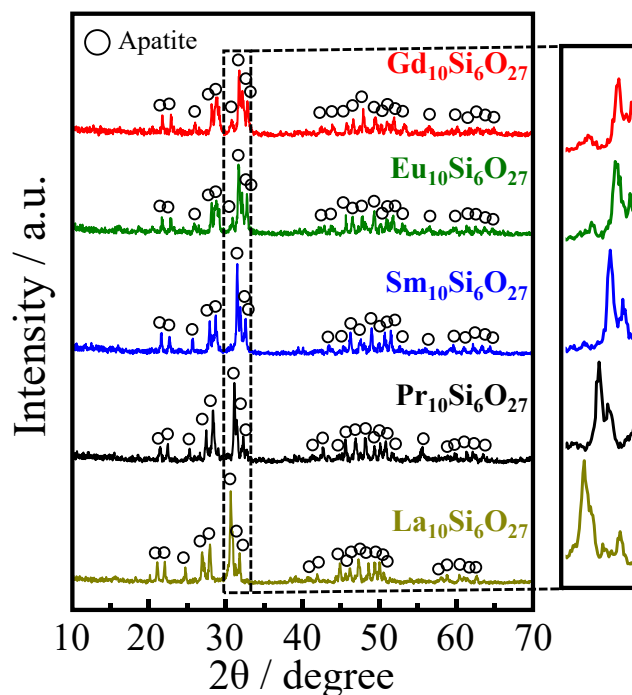
Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> (Ln = La, Pr, Eu, Sm, and Gd) promoters were prepared by a sol–gel process identical to that described in Chapter 1, using the corresponding Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Shin-Etsu Chemical Co., Ltd.). The γ-Al<sub>2</sub>O<sub>3</sub> support was loaded by ball milling, and the PdO primary catalyst was

introduced by impregnation to obtain 11.3 wt.% PdO/20 wt.%  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}$ ) catalysts.

In addition to the characterization methods employed in Chapter 1 (XRD, XRF, BET surface area analysis,  $\text{H}_2$ -TPR, and  $\text{CH}_4$  oxidation activity measurements), differential scanning calorimetry (DSC; NEXTA DSC 200, Hitachi) was conducted to determine specific heat capacities in the temperature range of 50–360 °C at a heating rate of 10 °C·min<sup>-1</sup> under a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe II, ULVAC-PHI) measurements were performed at ambient temperature using Al K $\alpha$  radiation. Binding energies were calibrated using the C 1s peak at 284.6 eV, and spectral fitting was carried out with Shirley background subtraction and Gaussian–Lorentzian functions.

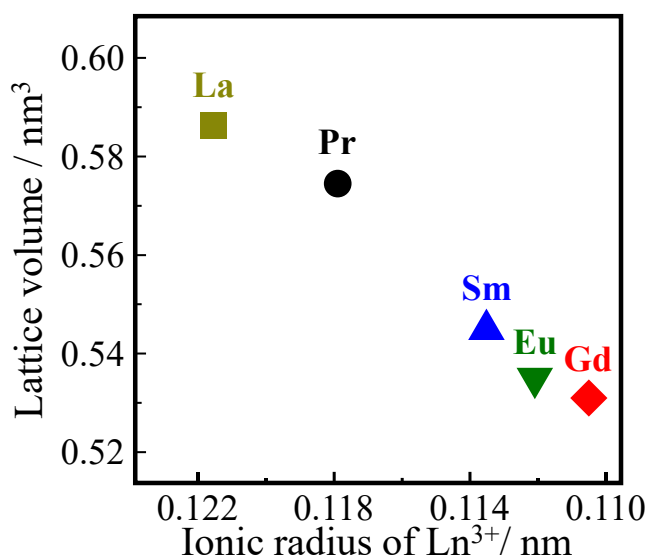
## 2.3. Results and Discussion

XRD analysis confirmed that all synthesized apatite-type silicate promoters,  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}$ ), exhibited only characteristic diffraction peaks of the apatite structure (Figure 2.1).



**Figure 2.1** XRD patterns of the  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}$ ).

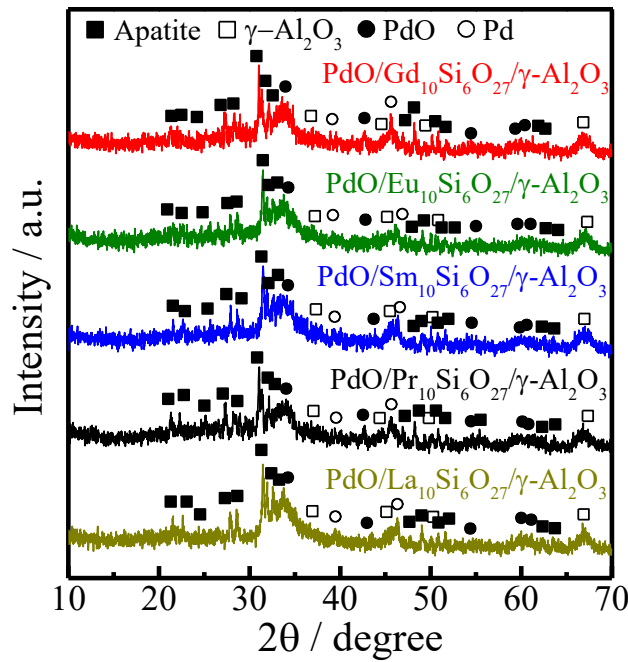
The diffraction peaks systematically shifted to higher angles with increasing lanthanoid atomic number, reflecting lattice contraction caused by decreasing ionic radii ( $\text{La}^{3+}$ : 0.1216 nm,  $\text{Pr}^{3+}$ : 0.1179 nm,  $\text{Sm}^{3+}$ : 0.1132 nm,  $\text{Eu}^{3+}$ : 0.1120 nm,  $\text{Gd}^{3+}$ : 0.1107 nm, CN = 9) [33]. Lattice parameters estimated using  $\alpha\text{-Al}_2\text{O}_3$  as an internal standard confirmed this trend, with lattice volumes decreasing from La to Gd ( $\text{La}_{10}\text{Si}_6\text{O}_{27}$ : 0.586 nm<sup>3</sup>,  $\text{Pr}_{10}\text{Si}_6\text{O}_{27}$ : 0.575 nm<sup>3</sup>,  $\text{Sm}_{10}\text{Si}_6\text{O}_{27}$ : 0.544 nm<sup>3</sup>,  $\text{Eu}_{10}\text{Si}_6\text{O}_{27}$ : 0.536 nm<sup>3</sup>,  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$ : 0.531 nm<sup>3</sup>; Figure 2.2). These results demonstrate the successful synthesis of phase-pure  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}$  promoters without secondary phases.



**Figure 2.2** Relationship between lanthanoid ionic radius and lattice volume of the  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}$  (Ln = La, Pr, Sm, Eu, Gd).

Figure 2.3 shows the XRD patterns of  $\text{PdO/Ln}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  (Ln = La, Pr, Sm, Eu, Gd) catalysts. Only diffraction peaks corresponding to apatite-type  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}$ , PdO, Pd, and  $\gamma\text{-Al}_2\text{O}_3$  were observed, confirming phase purity for all compositions.

The actual Pd loadings determined by XRF analysis were 12.40 wt.% (Ln = La), 11.11 wt.% (Ln = Pr), 12.42 wt.% (Ln = Sm), 12.94 wt.% (Ln = Eu), and 13.92 wt.% (Ln = Gd), which closely matched the intended stoichiometric values. These results indicate that the preparation method reliably produced  $\text{PdO/Ln}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalysts with reproducible compositions and structures.



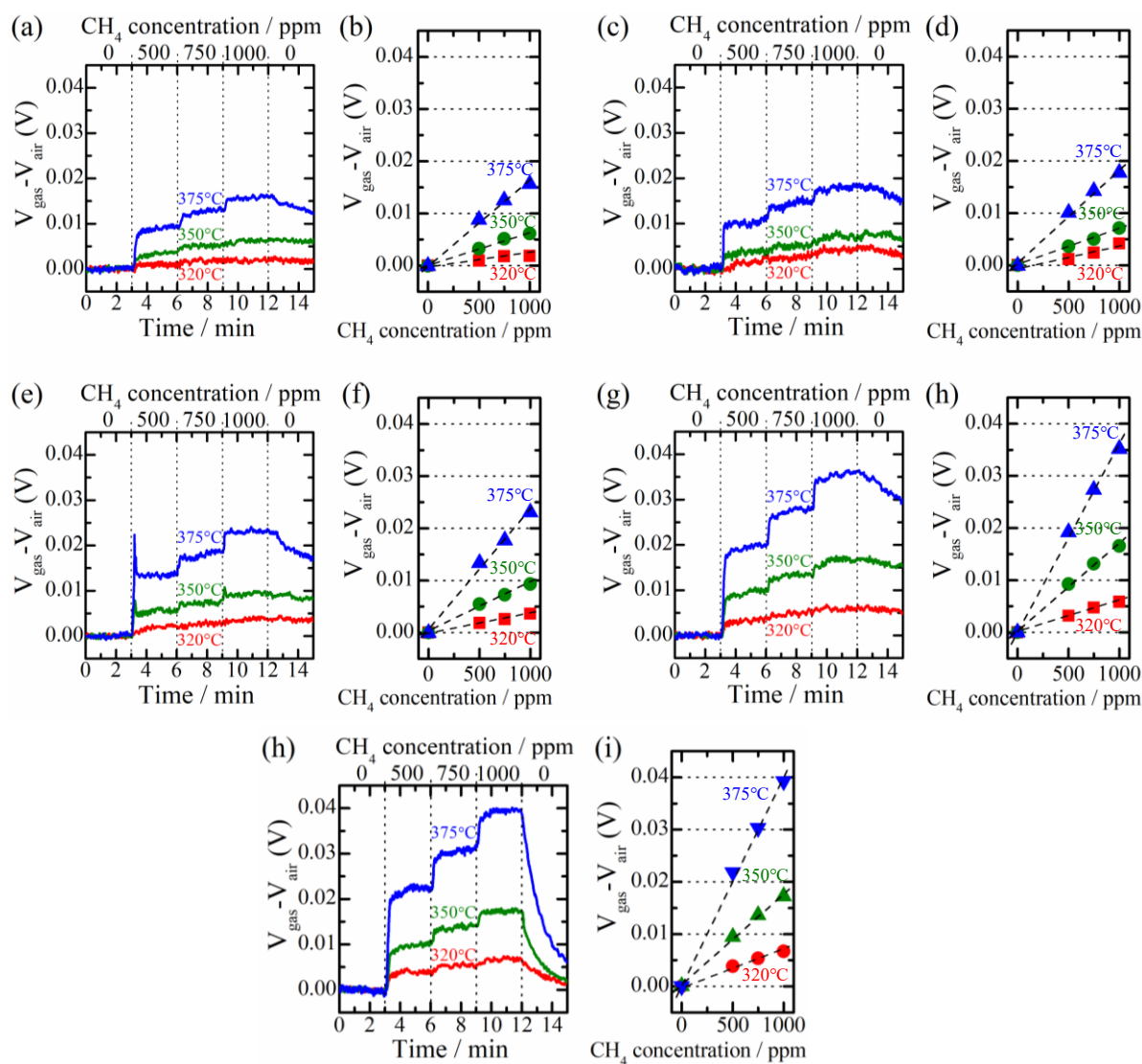
**Figure 2.3** XRD patterns of the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

Previous studies have reported that oxide-ion conductivity of apatite-type Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoters decreases systematically with increasing lanthanoid atomic number owing to lattice contraction associated with the lanthanoid contraction effect: La<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> ( $4.3 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ ) > Pr<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> ( $2.8 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ ) > Sm<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> ( $3.8 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ ) > Eu<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> ( $4.7 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ ) > Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> ( $1.2 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ ) at 500 °C [34]. Based on these values, La<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> would be expected to provide superior oxygen supply to PdO compared with Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>, and thus a sensor using La<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>-based catalysts might be anticipated to exhibit enhanced low-temperature CH<sub>4</sub> sensing performance.

The CH<sub>4</sub> sensing properties of catalytic combustion-type sensors employing PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) were evaluated in the CH<sub>4</sub> concentration range of 0–1000 ppm. Figure 2.4 presents representative response curves and sensor outputs measured at 320–375 °C, and Table 2.1 summarizes T<sub>50</sub> response times, sensor outputs at 1000 ppm CH<sub>4</sub>, and coefficients of determination (R<sup>2</sup>). All sensors exhibited highly linear relationships between sensor output and CH<sub>4</sub> concentration, with R<sup>2</sup> values exceeding 0.990 at operating temperatures of 350 °C or

higher. Response times were consistently fast (approximately 10 s) for all promoter compositions, with minimal variation.

Notably, the  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  sensor achieved quantitative  $\text{CH}_4$  detection ( $R^2 > 0.990$ ) at 320 °C, whereas sensors employing  $\text{La}_{10}\text{Si}_6\text{O}_{27}$ ,  $\text{Pr}_{10}\text{Si}_6\text{O}_{27}$ ,  $\text{Sm}_{10}\text{Si}_6\text{O}_{27}$ , or  $\text{Eu}_{10}\text{Si}_6\text{O}_{27}$  exhibited continuous output increases that did not follow  $\text{CH}_4$  concentration changes at this temperature. Furthermore, the sensor output at 1000 ppm  $\text{CH}_4$  increased systematically with lanthanoid atomic number and reached a maximum for the  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$ -based catalyst. These results demonstrate that



**Figure 2.4** Response curves and the sensor outputs of the sensors using  $\text{PdO}/\text{Ln}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalyst ( $\text{Ln} = \text{La}$  (a, b),  $\text{Pr}$  (c, d),  $\text{Sm}$  (e, f),  $\text{Eu}$  (g, h),  $\text{Gd}$  (i, j)) at various temperatures.

**Table 2.1** Sensing properties of the sensors using PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalyst toward CH<sub>4</sub>.

| Ln | Temperature / °C | R <sup>2</sup> | T <sub>50</sub> / s | Sensor output for 1000 ppm CH <sub>4</sub> / V |
|----|------------------|----------------|---------------------|------------------------------------------------|
| La | 350              | 0.993          | 9                   | 0.0061                                         |
|    | 375              | 0.994          | 13                  | 0.0156                                         |
| Pr | 350              | 0.997          | 9                   | 0.0072                                         |
|    | 375              | 0.993          | 10                  | 0.0178                                         |
| Sm | 350              | 0.990          | 8                   | 0.0093                                         |
|    | 375              | 0.992          | 7                   | 0.0231                                         |
| Eu | 350              | 0.995          | 12                  | 0.0166                                         |
|    | 375              | 0.997          | 11                  | 0.0352                                         |
| Gd | 320              | 0.993          | 13                  | 0.0067                                         |
|    | 350              | 0.997          | 13                  | 0.0173                                         |
|    | 375              | 0.996          | 11                  | 0.0393                                         |

Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> provides the most effective low-temperature sensing performance among the examined Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoters, indicating that sensor performance is governed not by bulk oxide-ion conductivity but by other physicochemical factors arising in the composite catalysts.

One potential factor influencing sensor performance is specific heat capacity, which determines the efficiency of heat transfer from catalytic combustion to the Pt coil. According to the heat capacity relationship  $Q = mc\Delta T$ , a lower specific heat capacity facilitates a faster temperature rise, shorter response time, and higher sensor output [35]. Because lanthanoid atomic mass increases with atomic number (La: 138.9 u, Pr: 140.9 u, Sm: 150.4 u, Eu: 151.96 u, Gd: 157.25 u), the specific heat capacity of Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoters was expected to decrease from La<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> to Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>. However, as shown in Table 2.2, all PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts exhibited similar specific heat capacities (approximately 80 J·mol<sup>-1</sup>·K<sup>-1</sup>), consistent with the nearly identical T<sub>50</sub> values observed for all sensors (Table 2.1).

**Table 2.2** Specific heat capacity of the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

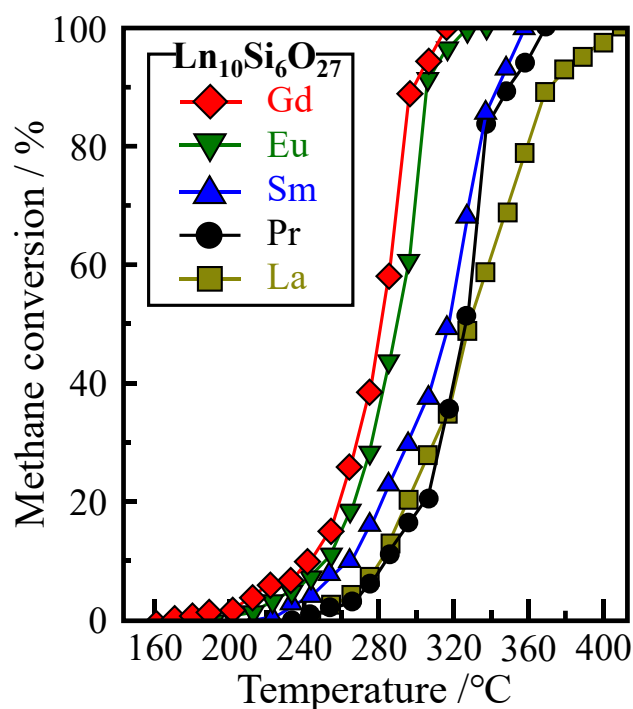
| Ln | Specific heat / J·mol <sup>-1</sup> ·K <sup>-1</sup> |
|----|------------------------------------------------------|
| La | 83.35                                                |
| Pr | 85.59                                                |
| Sm | 82.60                                                |
| Eu | 78.54                                                |
| Gd | 80.17                                                |

The effect of catalytic activity was then examined. A larger specific surface area generally provides more active sites for gas–catalyst interactions, enhancing oxidation efficiency and heat generation [36, 37]. However, the BET surface areas of PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts were similar (approximately 90–100 m<sup>2</sup>·g<sup>-1</sup>; Table 2.3), and the γ-Al<sub>2</sub>O<sub>3</sub> support dominated the surface area contribution (see Table 1.3). Therefore, differences in surface area cannot explain the observed change in sensing performance.

**Table 2.3** BET surface area of the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

| Ln | BET surface area / m <sup>2</sup> ·g <sup>-1</sup> |
|----|----------------------------------------------------|
| La | 101.05                                             |
| Pr | 91.32                                              |
| Sm | 87.75                                              |
| Eu | 85.75                                              |
| Gd | 98.81                                              |

In contrast, CH<sub>4</sub> oxidation activity measurements (Figure 2.5 and Table 2.4) revealed significant differences among the catalysts. Although all PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> achieved complete CH<sub>4</sub> conversion, PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> exhibited the lowest onset temperature (160 °C) and complete conversion temperature (310 °C). Higher catalytic activity promotes more efficient heat generation during CH<sub>4</sub> oxidation, directly enhancing sensor output. The strong correlation between



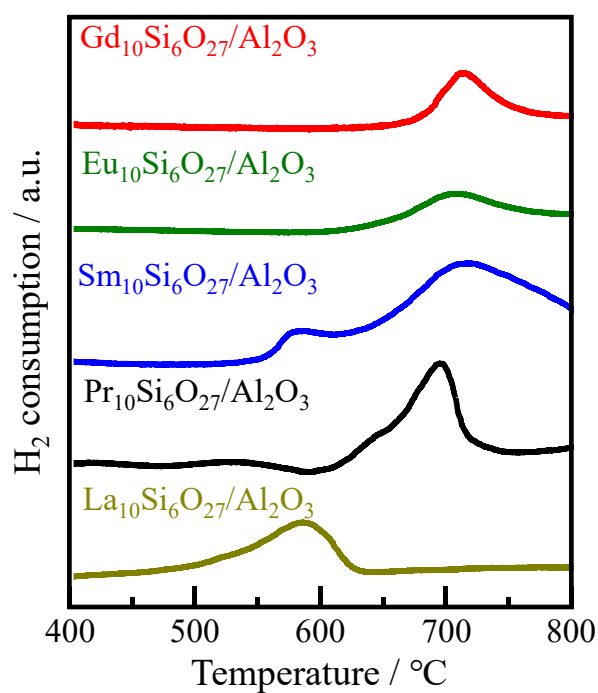
**Figure 2.5** Temperature dependence of CH<sub>4</sub> conversion for the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

**Table 2.4** CH<sub>4</sub> conversion onset and complete temperatures of the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

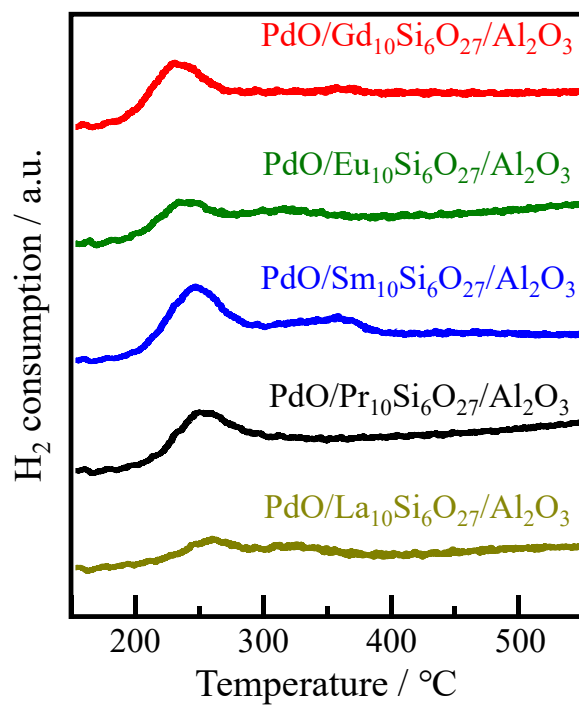
| Ln | Conversion onset Temperature / °C | Conversion complete Temperature / °C |
|----|-----------------------------------|--------------------------------------|
| La | 240                               | 400                                  |
| Pr | 230                               | 360                                  |
| Sm | 200                               | 350                                  |
| Eu | 190                               | 330                                  |
| Gd | 160                               | 310                                  |

catalytic activity and sensor sensitivity indicates that oxygen supply capability at the PdO–Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> interface, rather than bulk oxide-ion conductivity, governs overall sensor performance.

To further investigate oxygen supply capability, H<sub>2</sub>-TPR measurements were conducted. Figure 2.6 shows H<sub>2</sub>-TPR profiles of Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) promoters. La<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> exhibited the lowest reduction temperature, consistent with its highest oxide-ion conductivity,



**Figure 2.6** H<sub>2</sub>-TPR profiles of the Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) promoters.



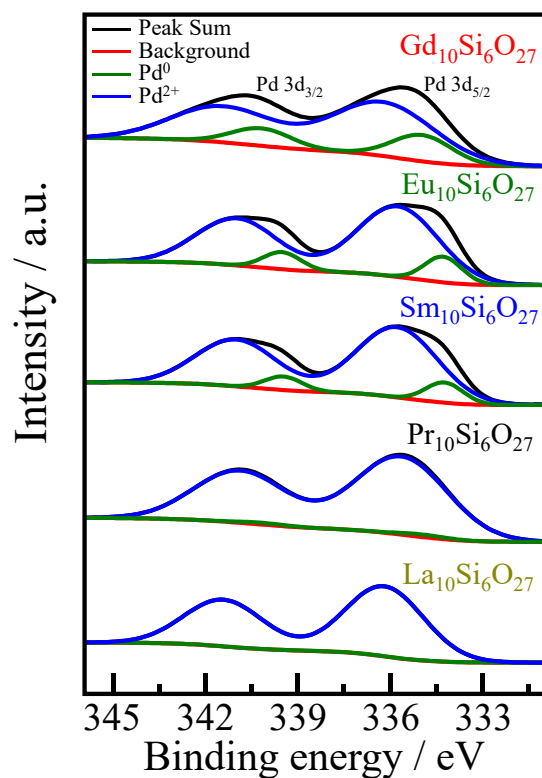
**Figure 2.7** H<sub>2</sub>-TPR profiles of the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

indicating superior low-temperature oxygen release. In contrast, PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts (Figure 2.7) displayed reduction peaks that systematically shifted to lower temperatures with increasing lanthanoid atomic number. The PdO/Gd Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the lowest reduction temperature among all compositions (Table 2.5), mirroring the trend observed in CH<sub>4</sub> sensing performance. These contrasting trends suggest that oxygen species released from Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> during PdO loading and calcination steps influenced the Pd/PdO formation ratio, thereby altering the oxygen release capacity of the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst.

**Table 2.5** H<sub>2</sub>-TPR peak temperature of the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

| Ln | Peak maximum Temperature / °C |
|----|-------------------------------|
| La | 286.0                         |
| Pr | 285.2                         |
| Sm | 271.5                         |
| Eu | 265.9                         |
| Gd | 254.4                         |

To clarify the Pd species responsible for this behavior, XPS analysis was performed. Figure 2.8 shows XPS spectra of PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts, revealing the coexistence of Pd<sup>2+</sup> and Pd<sup>0</sup> species. The Pd<sup>2+</sup> fraction, defined as Pd<sup>2+</sup>/(Pd<sup>2+</sup> + Pd<sup>0</sup>), decreased systematically from Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> (99.7%) to Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> (77.8%), whereas PdO/γ-Al<sub>2</sub>O<sub>3</sub> without a promoter exhibited the lowest Pd<sup>2+</sup> fraction (50.1%) (Table 2.6). These results indicate that La<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoters stabilize Pd<sup>2+</sup> species during catalyst preparation, with La<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> creating a highly oxidizing environment and Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> yielding a more balanced Pd<sup>2+</sup>/Pd<sup>0</sup> distribution.



**Figure 2.8** XPS spectra of the Pd 3d levels for the PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

**Table 2.6** Pd<sup>2+</sup>/(Pd<sup>0</sup> + Pd<sup>2+</sup>) ratio in PdO/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts.

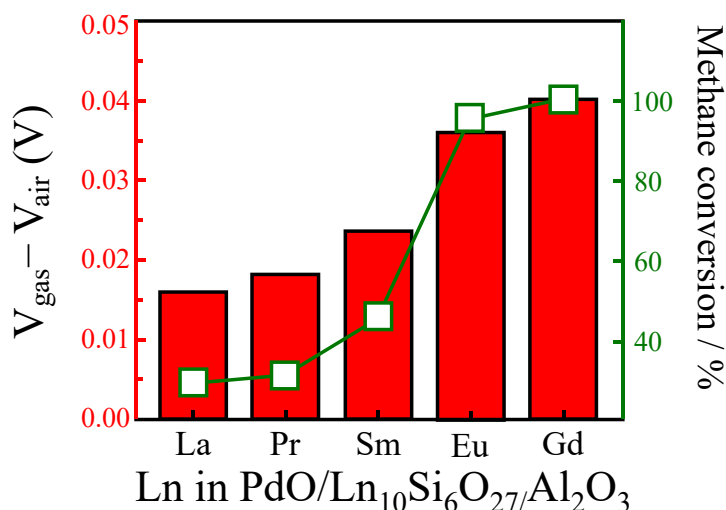
| Catalyst                                                                               | Pd <sup>2+</sup> /(Pd <sup>0</sup> + Pd <sup>2+</sup> ) / % |
|----------------------------------------------------------------------------------------|-------------------------------------------------------------|
| PdO/La <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 99.7                                                        |
| PdO/Pr <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 98.3                                                        |
| PdO/Sm <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 90.6                                                        |
| PdO/Eu <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 85.6                                                        |
| PdO/Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 77.8                                                        |
| PdO/γ-Al <sub>2</sub> O <sub>3</sub>                                                   | 50.1                                                        |

Sustained oxygen release requires redox cycling between  $\text{Pd}^{2+}$  and  $\text{Pd}^0$ , as described by Eq. (2-1):



Although  $\text{Pd}^{2+}$  acts as the active oxygen-releasing species, excessive  $\text{Pd}^{2+}$  forms strong  $\text{Pd}^{2+}\text{--O}$  bonds that suppress reduction and delay oxygen release. Conversely, metallic  $\text{Pd}^0$  donates electrons to adjacent  $\text{Pd}^{2+}$  species, weakening  $\text{Pd}\text{--O}$  bonds and lowering the activation energy for oxygen release; however, excessive  $\text{Pd}^0$  lacks oxygen supply capacity and disrupts re-oxidation [38–41]. Therefore, an optimal  $\text{Pd}^{2+}/\text{Pd}^0$  ratio is required. The  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalyst maintains this optimal balance, forming weakly bound  $\text{Pd}^{2+}\text{--O}$  species and enabling efficient low-temperature oxygen release [30, 31], thereby enhancing  $\text{CH}_4$  sensing performance. In contrast,  $\text{PdO}/\text{La}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$ , with an excessive  $\text{Pd}^{2+}$  fraction, forms strongly bound bulk  $\text{Pd}^{2+}\text{--O}$  species, which elevates the oxygen release temperature and degrades sensor performance.

Figure 2.9 correlates  $\text{CH}_4$  conversion at 310 °C with sensor output at 350 °C for  $\text{PdO}/\text{Ln}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalysts. Sensor output increases with increasing  $\text{CH}_4$  conversion, indicating that higher catalytic activity enhances combustion heat generation. The  $\text{PdO}/\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$



**Figure 2.9** Sensor output value for 1000 ppm  $\text{CH}_4$  at 350 °C of the sensors using the  $\text{PdO}/\text{Ln}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}$ ) catalysts and  $\text{CH}_4$  conversion rate at 310 °C for catalysts.

catalyst exhibited both the highest CH<sub>4</sub> conversion and the largest sensor output, consistent with its optimized Pd oxidation state and oxygen release behavior.

## 2.4. Conclusion

In this chapter, 11.3 wt.% PdO/20 wt.% Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts with different promoter compositions were synthesized, and their catalytic properties and CH<sub>4</sub> sensing performance were systematically evaluated. Although Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> exhibits the lowest bulk oxide-ion conductivity, its interaction with PdO optimizes the Pd<sup>2+</sup>/Pd<sup>0</sup> ratio, enabling efficient redox cycling and the formation of weakly bound Pd<sup>2+</sup>-O species. As a result, catalytic combustion-type sensors employing PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> exhibited the highest sensor output and the lowest operating temperature among the compositions investigated.

## Chapter 3

# Catalytic Combustion-Type Methane Gas Sensor with Tungsten-Doped Apatite-Type Gadolinium Silicate

### 3.1. Introduction

Chapters 1 and 2 demonstrated that  $\text{Ln}_{10}\text{Si}_6\text{O}_{27}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}$ ) promoters improved  $\text{CH}_4$  detection performance through enhanced low-temperature oxygen-release ability and increased  $\text{CH}_4$  catalytic activity. In particular, the 11.3 wt.% PdO/20 wt.%  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}/\gamma\text{-Al}_2\text{O}_3$  catalyst, which exhibits an optimal  $\text{Pd}^{2+}/\text{Pd}^0$  ratio for efficient redox cycling while forming weakly bound  $\text{Pd}^{2+}\text{-O}$  species, enabled both high combustion activity and low-temperature operation.

However, sensor performance is influenced not only by catalytic activity but also by thermal transport properties, such as specific heat capacity and specific surface area. Therefore, in this chapter, the reduction of specific heat capacity was targeted as a key factor to further enhance the  $\text{CH}_4$  sensing performance of catalytic combustion-type sensors employing  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$ . According to the heat capacity relationship  $Q = mc\Delta T$ , where  $Q$  is heat energy,  $m$  is mass,  $c$  is specific heat capacity, and  $\Delta T$  is temperature change, a lower specific heat capacity enables a faster temperature rise for a given heat input [35].

In solid materials, specific heat capacity is fundamentally governed by the number of vibrational degrees of freedom in the crystal lattice. Strong interatomic bonding or lattice distortion can restrict these vibrations, thereby reducing heat storage capacity. Based on this principle,  $\text{W}^{6+}$  ions were introduced into  $\text{Si}^{4+}$  sites of  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  to form stronger W–O bonds (approximately  $700\text{--}800\text{ kJ}\cdot\text{mol}^{-1}$ ) than Si–O bonds (approximately  $450\text{--}500\text{ kJ}\cdot\text{mol}^{-1}$ ), thereby suppressing atomic vibrations and reducing the specific heat capacity of the promoter [42, 43]. Accordingly, 11.3 wt.% PdO/20 wt.%  $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}/\gamma\text{-Al}_2\text{O}_3$  catalysts ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) were synthesized, and the  $\text{CH}_4$  sensing performance of catalytic combustion-type sensors employing these catalysts was evaluated.

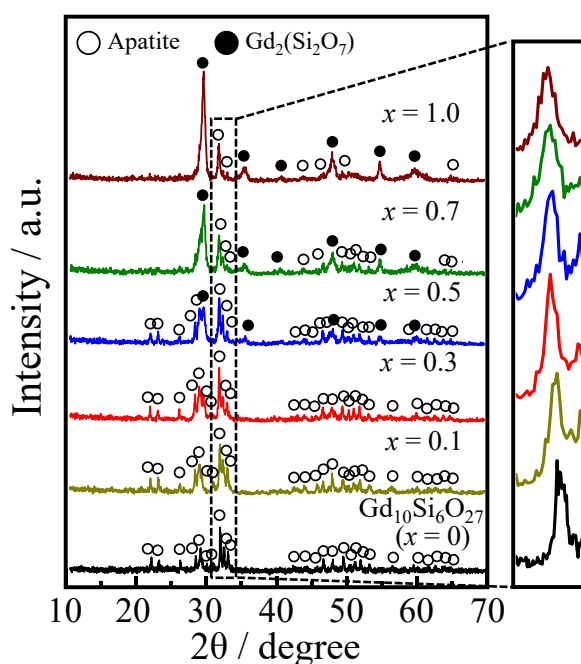
### 3.2. Experimental Procedure

The experimental procedures in Chapter 3 followed those established in Chapters 1 and 2, with the only modification being the introduction of a tungsten precursor for W doping. Specifically,  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 6\text{H}_2\text{O}$  (Kishida Chemical) was dissolved in deionized water and added together with the starting materials ( $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) during the sol–gel synthesis. The  $\gamma\text{-Al}_2\text{O}_3$  support was loaded by ball milling, and PdO was introduced by an impregnation method identical to those described previously, yielding  $\text{PdO}/\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}/\gamma\text{-Al}_2\text{O}_3$  ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) catalysts.

Characterization methods employed in the previous chapters (XRD, XRF, DSC, and  $\text{CH}_4$  oxidation activity measurements) were used. In addition, Raman spectroscopy was performed using a 532 nm laser (NRS-3100, Jasco) at 100 mW to analyze chemical bonding states and lattice vibrations.

### 3.3. Results and Discussion

Figure 3.1 shows the XRD patterns of  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  and  $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}$  ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ). A single-phase hexagonal apatite-type structure was obtained for  $x \leq 0.3$ , and diffraction peaks



**Figure 3.1** XRD patterns of the  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  and  $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}$  ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ).

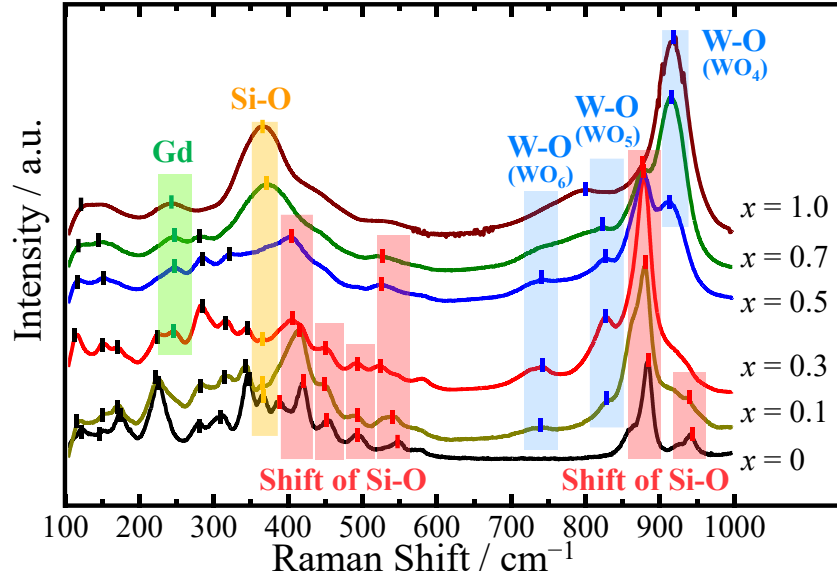
gradually shifted toward lower angles with increasing  $x$ , indicating substitution of  $\text{Si}^{4+}$  (0.04 nm) by larger  $\text{W}^{6+}$  ions (0.06 nm) [33]. In contrast, for  $x \geq 0.5$ , a secondary  $\text{Gd}_2(\text{Si}_2\text{O}_7)$  phase appeared together with the apatite phase, suggesting that excessive  $\text{W}^{6+}$  incorporation destabilizes the host lattice due to charge imbalance.

Because XRD alone cannot directly confirm W incorporation, the chemical compositions of the synthesized  $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}$  promoters were verified by XRF analysis. As summarized in Table 3.1, the measured W contents closely matched the target stoichiometries, confirming successful incorporation of tungsten.

**Table 3.1** Measured compositions of the  $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}$  ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ).

| Promoters                                                         | Measured composition                                                |
|-------------------------------------------------------------------|---------------------------------------------------------------------|
| $\text{Gd}_{10}\text{Si}_{5.9}\text{W}_{0.1}\text{O}_{27+\delta}$ | $\text{Gd}_{10}\text{Si}_{5.89}\text{W}_{0.11}\text{O}_{27+\delta}$ |
| $\text{Gd}_{10}\text{Si}_{5.7}\text{W}_{0.3}\text{O}_{27+\delta}$ | $\text{Gd}_{10}\text{Si}_{5.73}\text{W}_{0.27}\text{O}_{27+\delta}$ |
| $\text{Gd}_{10}\text{Si}_{5.5}\text{W}_{0.5}\text{O}_{27+\delta}$ | $\text{Gd}_{10}\text{Si}_{5.57}\text{W}_{0.43}\text{O}_{27+\delta}$ |
| $\text{Gd}_{10}\text{Si}_{5.3}\text{W}_{0.7}\text{O}_{27+\delta}$ | $\text{Gd}_{10}\text{Si}_{5.41}\text{W}_{0.59}\text{O}_{27+\delta}$ |
| $\text{Gd}_{10}\text{Si}_{5.0}\text{W}_{1.0}\text{O}_{27+\delta}$ | $\text{Gd}_{10}\text{Si}_{4.99}\text{W}_{1.01}\text{O}_{27+\delta}$ |

Raman spectroscopy provided complementary insight into  $\text{W}^{6+}$  bonding and lattice incorporation (Figure 3.2). The Raman spectra exhibited characteristic vibrational bands associated with Si–O and Gd–O bonding environments (assignments are listed in Table 3.2 [44–54]). In the low-frequency region ( $< 350 \text{ cm}^{-1}$ ), bands related to external translational and librational motions of Gd ions and  $\text{SiO}_4$  units were observed. These bands gradually weakened with increasing W content and eventually disappeared, indicating suppression of external lattice vibrations due to strong W–O bonding. A new Raman band appeared at  $240\text{--}245 \text{ cm}^{-1}$  for  $x \geq 0.3$ , which is attributed to Gd ion translational modes in the  $\text{Gd}_2(\text{Si}_2\text{O}_7)$  phase. Internal Si–O bending ( $350\text{--}600 \text{ cm}^{-1}$ ) and stretching ( $> 800 \text{ cm}^{-1}$ ) modes showed red shifts and peak broadening with increasing W content. This behavior is attributed to substitution of lighter Si atoms by heavier W atoms, which lowers vibrational frequencies



**Figure 3.2** Raman spectra of  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  and  $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}$  ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ).

**Table 3.2** Raman peak assignments for the  $\text{Gd}_{10}\text{Si}_6\text{O}_{27}$  and  $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}$  ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ).

| Raman shift ( $\text{cm}^{-1}$ ) of $\text{Gd}_{10}\text{Si}_{6-x}\text{W}_x\text{O}_{27+\delta}$ |       |       |       |       |       | Assigned Mode                                             | References       |
|---------------------------------------------------------------------------------------------------|-------|-------|-------|-------|-------|-----------------------------------------------------------|------------------|
| 0                                                                                                 | 0.1   | 0.3   | 0.5   | 0.7   | 1.0   |                                                           |                  |
| 121                                                                                               | 117.2 | 111.7 | 114.9 | 122.5 | 126.9 | Translations and librations of Gd ions                    | [44, 46]         |
| 147                                                                                               | 148.9 | 147.1 | 149.2 | 148.1 | -     | Translations and librations of Gd ions                    | [44, 46]         |
| 171.1                                                                                             | 168   | 167   | -     | -     | -     | Translations and librations of Gd ions                    | [44, 45, 47, 48] |
| 222.6                                                                                             | 221.6 | 223.4 | -     | -     | -     | Translations and librations of $\text{SiO}_4$             | [44, 45, 47]     |
| -                                                                                                 | -     | 241.2 | 242.5 | 243.3 | 241.9 | Translations and librations of Gd ions                    | [44, 46, 47]     |
| 276.7                                                                                             | 281.2 | 281.7 | 281.5 | 276.9 | -     | Translations and librations of Gd ions                    | [44, 47, 49]     |
| 309.4                                                                                             | 312.7 | 313.2 | 312.5 | -     | -     | Translations and librations of Gd ions                    | [44, 45]         |
| 344.2                                                                                             | 340.6 | 342.9 | -     | -     | -     | Translations and librations of Gd ions and $\text{SiO}_4$ | [44, 45, 49]     |
| 364.3                                                                                             | 366.1 | 366.4 | -     | 368.7 | 364.6 | Bending modes of Si-O ( $\text{SiO}_4$ )                  | [47, 49]         |
| 386.1                                                                                             | -     | -     | -     | -     | -     | Bending modes of Si-O ( $\text{SiO}_4$ )                  | [47, 48, 50]     |
| 417.5                                                                                             | 413.5 | 403.2 | 400.1 | -     | -     | Bending modes of Si-O ( $\text{SiO}_4$ )                  | [45, 47, 52]     |
| 454.1                                                                                             | 438.4 | 438.9 | -     | -     | -     | Bending modes of Si-O ( $\text{SiO}_4$ )                  | [50, 52]         |
| 492.1                                                                                             | 485.9 | 488.8 | -     | -     | -     | Bending modes of Si-O ( $\text{SiO}_4$ )                  | [50, 52]         |
| 547                                                                                               | 536   | 521.5 | 523.3 | 519.3 | -     | Bending modes of Si-O ( $\text{SiO}_4$ )                  | [45, 48, 50, 52] |
| -                                                                                                 | 739.3 | 742.2 | 741.7 | -     | -     | Stretching modes of W-O ( $\text{WO}_6$ )                 | [51, 53, 54]     |
| -                                                                                                 | 829.8 | 830.3 | 829.4 | 827.1 | 801.3 | Stretching modes of W-O ( $\text{WO}_5$ )                 | [49, 54]         |
| 886                                                                                               | 881.9 | 880.9 | 879.9 | 880   | -     | Stretching modes of Si-O ( $\text{SiO}_4$ )               | [45, 47, 48]     |
| -                                                                                                 | -     | -     | 916.4 | 916.5 | 921.1 | Stretching modes of W-O ( $\text{WO}_4$ )                 | [53, 54]         |
| 943.9                                                                                             | 939.3 | -     | -     | -     | -     | Stretching modes of Si-O ( $\text{SiO}_4$ )               | [45, 47, 48]     |

and introduces diverse bonding environments through W–O bond formation. The Si–O bending band near 360–370 cm<sup>−1</sup> gradually weakened and disappeared at  $x = 0.5$ , indicating local structural distortion of the Si–O network. At higher W contents ( $x \geq 0.7$ ), a broad band reappeared in this region, suggesting the emergence of new vibrational modes associated with secondary-phase formation.

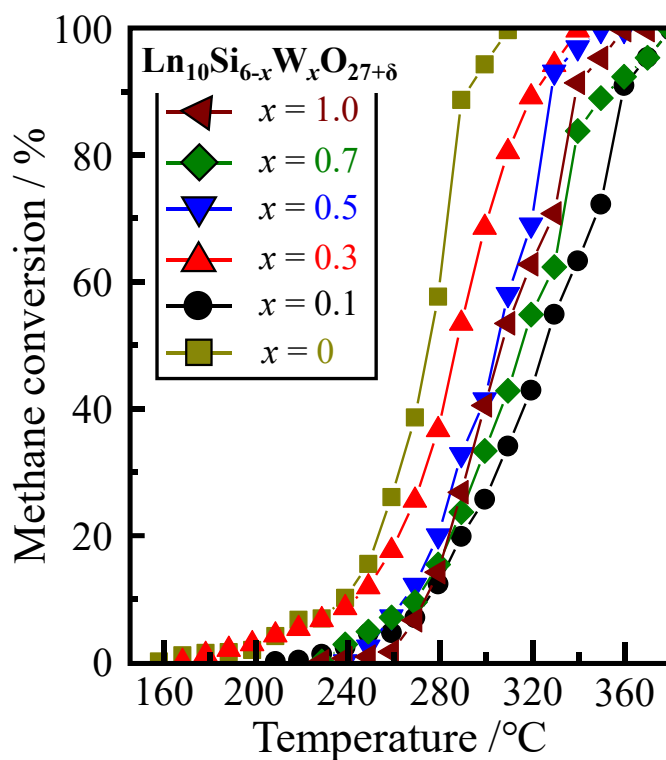
W–O bonding, which cannot be detected by XRD, was clearly identified by Raman spectroscopy. Bands corresponding to WO<sub>5</sub> (around 830 cm<sup>−1</sup>) and WO<sub>6</sub> (around 740 cm<sup>−1</sup>) coordination reached maximum intensity at  $x = 0.3$ , indicating that W is predominantly stabilized in these coordination environments within the apatite lattice. At  $x \geq 0.5$ , a new Raman band appeared in the 910–930 cm<sup>−1</sup> region. This is attributed to WO<sub>4</sub> species, suggesting that independent WO<sub>4</sub> units form within the secondary phase Gd<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>) or exist as isolated W-containing domains exceeding the W solubility limit within the apatite lattice. The W solubility limit in the apatite lattice is approximately  $x = 0.3$ .

Table 3.3 summarizes the specific heat capacities of PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) catalysts. Specific heat capacity decreased with increasing W content up to  $x = 0.3$ , which is attributed to suppression of atomic vibrations by strong W–O bonding. At higher doping levels ( $x \geq 0.5$ ), specific heat capacity increased again, likely due to the formation of heterogeneous interfacial regions that restore vibrational freedom.

**Table 3.3** Specific heat capacity of the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) catalysts.

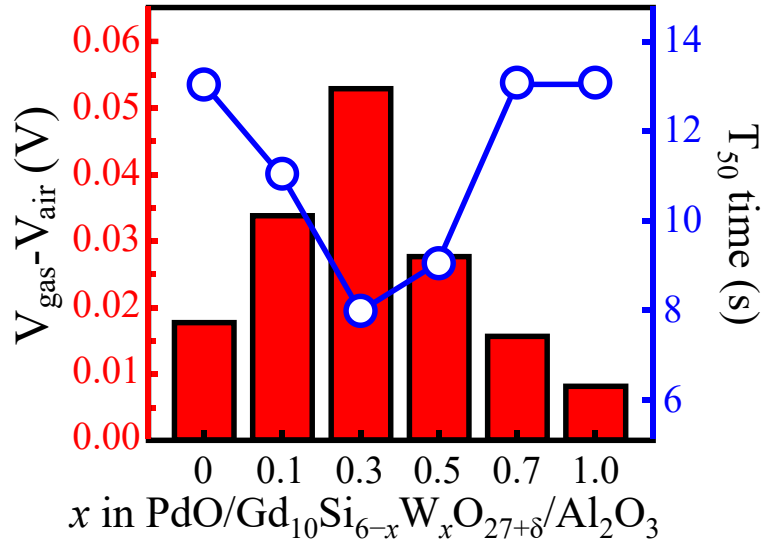
| Catalyst                                                                                                   | Specific heat / J·mol <sup>−1</sup> ·K <sup>−1</sup> |
|------------------------------------------------------------------------------------------------------------|------------------------------------------------------|
| PdO/Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub>                     | 80.17                                                |
| PdO/Gd <sub>10</sub> S <sub>5.9</sub> W <sub>0.1</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 32.93                                                |
| PdO/Gd <sub>10</sub> S <sub>5.7</sub> W <sub>0.3</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 19.54                                                |
| PdO/Gd <sub>10</sub> S <sub>5.5</sub> W <sub>0.5</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 25.61                                                |
| PdO/Gd <sub>10</sub> S <sub>5.3</sub> W <sub>0.7</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 67.62                                                |
| PdO/Gd <sub>10</sub> S <sub>5.0</sub> W <sub>1.0</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 67.27                                                |

As discussed in the General Introduction, optimal sensor performance requires a balance between catalytic activity and thermal transport properties. While W–O bond formation effectively reduces specific heat capacity, excessive W doping induces lattice distortion and secondary-phase formation, which likely reduces oxygen vacancy concentration and oxide-ion mobility. Consequently, oxygen supply from the promoter to PdO is diminished, leading to reduced CH<sub>4</sub> oxidation activity. Figure 3.3 shows the temperature dependence of CH<sub>4</sub> combustion activity for PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts. W doping increased both the CH<sub>4</sub> combustion onset temperature and the complete conversion temperature, indicating a trade-off between enhanced thermal responsiveness and catalytic activity.



**Figure 3.3** Temperature dependence of CH<sub>4</sub> conversion for the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) catalysts.

Figure 3.4 presents sensor outputs and 50% response times at 350 °C for 1000 ppm CH<sub>4</sub>, and Table 3.4 summarizes the lowest operating temperatures. With increasing W content up to  $x = 0.3$ ,

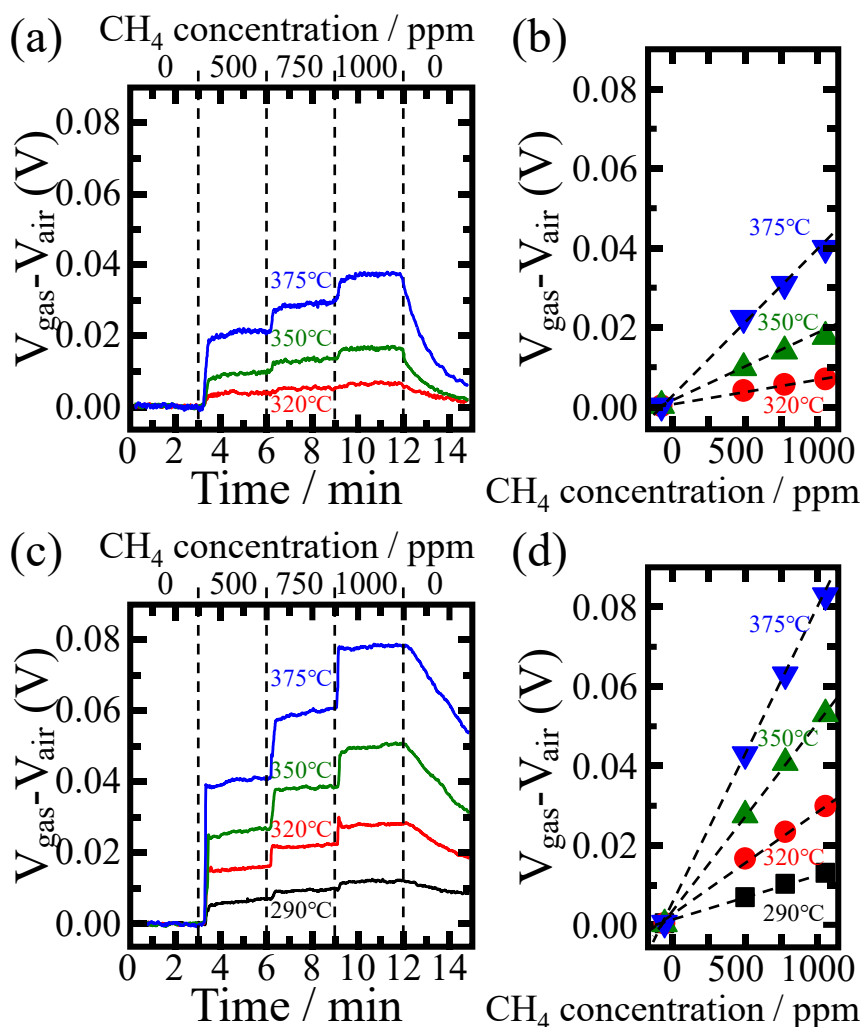


**Figure 3.4** Temperature dependence of CH<sub>4</sub> conversion for the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) catalysts.

**Table 3.4** Lowest operating temperature of the sensor using PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) catalysts.

| Sensor                                                                                                      | Operating temperature / °C |
|-------------------------------------------------------------------------------------------------------------|----------------------------|
| PdO/Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /γ-Al <sub>2</sub> O <sub>3</sub>                      | 320                        |
| PdO/Gd <sub>10</sub> Si <sub>5.9</sub> W <sub>0.1</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 290                        |
| PdO/Gd <sub>10</sub> Si <sub>5.7</sub> W <sub>0.3</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 290                        |
| PdO/Gd <sub>10</sub> Si <sub>5.5</sub> W <sub>0.5</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 320                        |
| PdO/Gd <sub>10</sub> Si <sub>5.3</sub> W <sub>0.7</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 350                        |
| PdO/Gd <sub>10</sub> Si <sub>5.0</sub> W <sub>1.0</sub> O <sub>27+δ</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | 350                        |

sensor output increased, response time shortened, and operating temperature decreased, reaching the best performance at  $x = 0.3$  with a minimum operating temperature of 290 °C. This improvement is attributed to the reduced specific heat capacity resulting from W<sup>6+</sup> doping outweighing the negative impact of diminished catalytic activity. In contrast, for  $x \geq 0.5$ , sensor output decreased, response time increased, and operating temperature rose with increasing  $x$ . This is attributed to heterogeneous interfacial regions elevating specific heat capacity, which impeded efficient heat transfer and suppressed temperature rise from CH<sub>4</sub> combustion.



**Figure 3.5** Response curves and sensor outputs of the sensors using PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (a, b) and PdO/Gd<sub>10</sub>Si<sub>5.7</sub>W<sub>0.3</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (c, d) catalyst at various temperatures.

**Table 3.5** Sensing properties of sensors using the PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>5.7</sub>W<sub>0.3</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts toward CH<sub>4</sub>.

| Sensor                                                                                                            | Temperature / °C | R <sup>2</sup> | T <sub>50</sub> / s | Sensor output for 1000 ppm CH <sub>4</sub> / V |
|-------------------------------------------------------------------------------------------------------------------|------------------|----------------|---------------------|------------------------------------------------|
| PdO/<br>Gd <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> /<br>γ-Al <sub>2</sub> O <sub>3</sub>                    | 320              | 0.993          | 13                  | 0.0067                                         |
|                                                                                                                   | 350              | 0.997          | 13                  | 0.0173                                         |
|                                                                                                                   | 375              | 0.996          | 11                  | 0.0393                                         |
| PdO/<br>Gd <sub>10</sub> Si <sub>5.7</sub> W <sub>0.3</sub> O <sub>27</sub> /<br>γ-Al <sub>2</sub> O <sub>3</sub> | 290              | 0.999          | 11                  | 0.0128                                         |
|                                                                                                                   | 320              | 0.996          | 8                   | 0.0297                                         |
|                                                                                                                   | 350              | 0.999          | 8                   | 0.0531                                         |
|                                                                                                                   | 375              | 0.999          | 9                   | 0.0831                                         |

Figure 3.5 shows representative response profiles and sensor outputs for sensors employing PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and PdO/Gd<sub>10</sub>Si<sub>5.7</sub>W<sub>0.3</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> under varying CH<sub>4</sub> concentrations. As summarized in Table 3.5, both sensors exhibited excellent linearity ( $R^2 \geq 0.990$ ) above 320 °C. Notably, the W-doped sensor exhibited a clear concentration-dependent response even at 290 °C, with a T<sub>50</sub> of 11 s, and showed more than twice the sensor output and a 2–5 s shorter response time than the undoped sensor under identical conditions.

### 3.4. Conclusion

In this chapter, the effect of W<sup>6+</sup> doping into the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter on catalyst properties and sensor performance was investigated using 11.3 wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts. Among the examined compositions, the sensor employing PdO/Gd<sub>10</sub>Si<sub>5.7</sub>W<sub>0.3</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> exhibited rapid and quantitative CH<sub>4</sub> detection at temperatures of 290 °C and above. This improvement originates from reduced specific heat capacity due to strong W–O bond formation, which provides an optimal balance between enhanced thermal responsiveness and preserved catalytic activity.

## ***Summary***

In this doctoral thesis, low-temperature operative catalytic combustion-type methane gas sensors employing apatite-type rare-earth silicate promoters were developed. Among the factors known to influence methane detection performance in catalytic combustion-type gas sensors, the effects of catalytic activity and thermal transport properties were systematically investigated through a series of experiments, and the key characteristics governing these factors were elucidated. The main results obtained in this study are summarized as follows.

### **Chapter 1**

To achieve stable low-temperature CH<sub>4</sub> detection in catalytic combustion-type gas sensors, an apatite-type Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter possessing oxide-ion mobility as well as excellent thermal and chemical stability was introduced into PdO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. This promoter enhanced low-temperature oxygen-release ability, thereby improving CH<sub>4</sub> oxidation activity. As a result, the sensor employing an 11.3 wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst generated greater combustion heat and enabled stable CH<sub>4</sub> detection at 320 °C, which is 115 °C lower than that of the sensor without the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter.

### **Chapter 2**

To elucidate the key factors underlying the superior performance of Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>-promoted sensors, the properties of 11.3 wt.% PdO/20 wt.% Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Ln = La, Pr, Sm, Eu, Gd) catalysts with different promoter compositions were systematically compared. Although the Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter exhibited the lowest bulk oxide-ion conductivity among the examined materials, its interaction with PdO optimized the Pd<sup>2+</sup>/Pd<sup>0</sup> ratio, enabling efficient redox cycling and the formation of weakly bound Pd<sup>2+</sup>-O species through moderate Pd<sup>2+</sup> stabilization. Consequently,

PdO/Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> sensors exhibited the highest sensor output and the lowest operating temperature among all Ln compositions.

### Chapter 3

To further enhance CH<sub>4</sub> sensing performance by improving thermal transport properties, W<sup>6+</sup> doping was introduced into Si<sup>4+</sup> sites of the optimal Gd<sub>10</sub>Si<sub>6</sub>O<sub>27</sub> promoter. This modification formed stronger W–O bonds, suppressing lattice vibrations and reducing specific heat capacity. Among the synthesized 11.3 wt.% PdO/20 wt.% Gd<sub>10</sub>Si<sub>6-x</sub>W<sub>x</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ( $x = 0.1, 0.3, 0.5, 0.7, 1.0$ ) catalysts, the solubility-limit composition ( $x = 0.3$ ) exhibited the lowest specific heat capacity due to suppressed lattice vibrations induced by strong W–O bonding. Consequently, PdO/Gd<sub>10</sub>Si<sub>5.7</sub>W<sub>0.3</sub>O<sub>27+δ</sub>/γ-Al<sub>2</sub>O<sub>3</sub> sensors achieved rapid and quantitative CH<sub>4</sub> detection at temperatures of 290 °C and above, with more than twofold improved sensitivity, a 2–5 s reduction in T<sub>50</sub>, and a lower operating temperature compared with the undoped counterpart.

Overall, these results demonstrate that achieving both balanced oxygen supply for optimal catalytic activity and enhanced thermal transport through lattice vibration suppression is an effective strategy for high-performance catalytic combustion-type methane gas sensors. From a catalytic activity perspective, promoter oxide-ion conductivity facilitates Pd<sup>2+</sup> formation and weak Pd<sup>2+</sup>–O bonding, enabling efficient low-temperature oxygen release and redox cycling during PdO loading. However, excessive bulk oxide-ion conductivity disrupts the Pd<sup>2+</sup>/Pd<sup>0</sup> balance by promoting strong Pd<sup>2+</sup>–O bonding, indicating that appropriately balanced oxide-ion conductivity is essential for optimal chemical-state control. In addition, dopant-induced suppression of lattice vibrations reduces specific heat capacity and accelerates heat transfer to the Pt coil, thereby enhancing sensor sensitivity and response. Conversely, excessive lattice modification leading to secondary-phase formation and reduced defect concentration degrades oxide-ion mobility and methane combustion activity, underscoring the importance of balancing catalytic activity and thermal transport properties. Thus, this

thesis establishes that optimal performance of catalytic combustion-type methane gas sensors requires integrated promoter–PdO interaction engineering for balanced oxygen supply and lattice-level thermal management via specific heat capacity reduction, providing valuable guidelines for next-generation sensor design.

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## ***List of Publications***

1. Novel Low-Temperature Operating Catalytic Combustion-Type Methane Gas Sensor Based on Gadolinium Silicate-Supported Palladium Oxide

**Wonjoon Lee**, Shinji Tamura, and Nobuhito Imanaka\*

The Institute of Electrical Engineers of Japan, **2025**, Online First.

2. Catalytic Combustion-Type Methane Gas Sensor with Tungsten-doped Apatite-type Gadolinium Silicate

**Wonjoon Lee**, Shinji Tamura, and Nobuhito Imanaka\*

Chemistry Letters, **2025**, *54*, upaf177.

3. Role of Apatite-Type Lanthanoid Silicate Promoter in PdO/Ln<sub>10</sub>Si<sub>6</sub>O<sub>27</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Catalysts for Catalytic Combustion-Type Methane Sensor: Contrasting Trends between Oxide-Ion Conductivity and Sensor Performance

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