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Letter

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

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In this study, a novel catalytic combustion-type methane gas sensor was developed using an 11.3 wt.% PdO/20 wt.% $Gd_{10}Si_6O_{27}/\gamma\text{-}Al_2O_3$ (PdO/GdSiO/AlO) catalyst. The incorporation of GdSiO as a promoter efficiently supplied active oxygen species to the PdO, thereby enabling methane combustion at low temperatures. The sensor employing the PdO/GdSiO/AlO catalyst exhibited a quantitative response to methane at temperatures as low as 320 °C, with a 50% response time of approximately 13 s. © 2025 The Author(s). *IEEJ Transactions on Electrical and Electronic Engineering* published by Institute of Electrical Engineers of Japan and Wiley Periodicals LLC.

Keywords: catalytic combustion-type gas sensor; methane; gadolinium silicate

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Introduction

Methane (CH_4) is a main component of natural gas widely used as an energy source; however, its greenhouse effect is 21 times greater than that of CO_2 [1]. Therefore, quantitative and real-time monitoring of CH_4 released into the atmosphere is crucial for mitigating global warming. Catalytic combustion-type sensors are promising tools for this purpose owing to their long-term stability and simple construction, comprising a Pt coil covered by a CH_4 oxidation catalyst [2]. The detection mechanism of this type of sensor relies on CH_4 oxidation by the catalyst, which generates combustion heat that changes the temperature of the Pt coil, causing a change in its electrical resistance (sensor output). Therefore, the oxidation activity of the catalyst strongly affects the sensor output. Because conventionally used PdO/γ-Al_2O_3 catalysts can use thermodynamically stable oxygen gas in the atmosphere for CH_4 oxidation, production of active oxygen species such as O^{2-} on PdO is difficult, thus requiring high temperatures above 450°C for complete CH_4 oxidation [3]. Therefore, incorporating a promoter capable of supplying active oxygen to PdO is essential for achieving low-temperature CH_4 oxidation.

In this study, an apatite-type gadolinium silicate ($Gd_{10}Si_6O_{27}$; GdSiO) was employed as a novel promoter material. Although various oxide ion conductors, such as Bi_2O_3-based oxides and Sm-doped CeO_2, have been investigated for low-temperature applications, the apatite-type structure of GdSiO exhibits high oxide ion conductivity even at temperatures as low as 300°C, along with excellent chemical stability. These properties make it a promising candidate for low-temperature CH_4 oxidation [4,5]. Therefore, we developed a catalytic combustion-type CH_4 gas sensor using an 11.3 wt.% PdO/20 wt.% $Gd_{10}Si_6O_{27}/\gamma\text{-}Al_2O_3$ (Expression in mol%: 11.59 mol% PdO/1.03 mol% $Gd_{10}Si_6O_{27}/\gamma\text{-}Al_2O_3$, denoted as PdO/GdSiO/AlO hereafter) catalyst and investigated its sensing performance.

Experiment

GdSiO was prepared using the sol–gel method. A stoichiometric mixture of $Gd(NO_3)_3{\cdot}6H_2O$ and $Si(OC_2H_5)_4$ was dissolved in deionized water to form a sol, and acetic acid was added to adjust the pH, resulting in gel formation. After stirring for 1 h at 25°C, the wet gel was heated at 350°C for 4 h. The resulting powder was calcined at 1000°C for 2 h. The product was mixed with AlO (weight ratio: 1:4) in ethanol by ball-milling and heated at 500°C for 4 h to load GdSiO onto AlO. PdO was loaded onto GdSiO/AlO via impregnation with $Pd(NO_2)_2(NH_3)_2$ solution to obtain the PdO/GdSiO/AlO catalyst, which was calcined at 500°C for 4 h.

The stability of the catalyst under a reducing atmosphere was evaluated using temperature-programmed reduction (TPR) under 5 vol.% H_2/Ar at a flow rate of 50 ml min^{-1} and a heating rate of 5°C min^{-1}. Methane oxidation activity was measured using a fixed-bed reactor with 1 vol.% CH_4 in air at a flow rate of 33.4 mL min^{-1} (SV: 20000 L kg^{-1} h^{-1}).

Sensor elements were fabricated by coating a Pt coil (1 mm length, 30 μm diameter) with catalyst by sintering the catalyst powder. Sensor performance was evaluated in a test chamber by applying a DC voltage to heat the Pt coil. The sensor signal ($V_{gas} - V_{air}$) was investigated by introducing methane gas (0–1000 ppm) into the chamber, where V_{gas} and V_{air} are sensor voltages in CH_4 and air, respectively.

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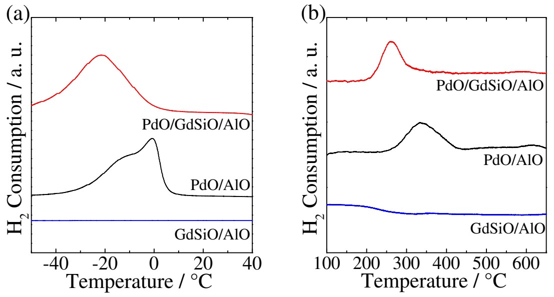

Fig. 1. H_2-TPR profiles of the PdO/GdSiO/AlO and PdO/AlO catalysts and the GdSiO/AlO promoter: (a) below 40°C and (b) above 100°C

Result and Discussion

To investigate the oxygen release ability of the PdO/GdSiO/AlO catalyst, which affects the sensing performance of catalytic combustion-type sensors, H_2-TPR measurements were conducted across low- and high-temperature regions. This was performed because PdO may contain two types of released oxygen, surface and lattice oxygen, which may be released at different temperatures. As shown in Fig. 1(a), reduction peaks related to the PdO surface can be observed for both PdO/GdSiO/AlO and PdO/AlO below 40°C [6]. In contrast, GdSiO/AlO exhibits no such peaks, thus indicating that the PdO surface was reduced by H_2. Moreover, the reduction onset and peak temperatures both decreased upon applying the GdSiO promoter, suggesting that it facilitated the reduction of the PdO surface. This phenomenon can be explained by the weakening of the Pd−O bond caused by oxygen vacancies in the promoter [7]. Owing to weakened Pd−O bonding, the PdO surface was easily reduced by H_2. Furthermore, all the solids show a reduction peak above 100°C, while GdSiO/γ-Al_2O_3 exhibits a broad, low-intensity peak, which may suggest gradual oxygen release from the GdSiO (Fig. 1(b)). Because γ-Al_2O_3 did not release lattice oxygen under the present experimental conditions, the reduction peak observed at approximately 300°C for the PdO-loaded solids can be attributed to the release of lattice oxygen from PdO [8]. As described above, oxygen vacancies in GdSiO can weaken the Pd−O bonds in PdO, causing the peak temperature related to the reduction of lattice oxygen in PdO to be lower. Thus, the H_2-TPR results indicate that the PdO/GdSiO/AlO catalyst can oxidize methane at lower temperatures than the PdO/AlO catalyst because the apatite-type GdSiO facilitates the oxygen release ability of the PdO/AlO catalyst.

Figure 2 shows the temperature dependence of methane oxidation activity of the catalysts. The PdO/GdSiO/AlO catalyst began oxidizing CH_4 above 160°C and achieved complete oxidation at 310°C. Complete oxidation of methane to CO_2 and H_2O was confirmed by GC−MS analysis. The PdO/GdSiO/AlO catalyst showed a lower CH_4 oxidation temperature than the PdO/AlO catalyst, thus indicating that the GdSiO solid acted as a promoter of the methane oxidation catalyst.

Figure 3 shows the response curves to methane concentration changes for the sensor employing the PdO/GdSiO/AlO catalyst at temperatures above 290°C, along with the sensor output at various CH_4 concentrations measured at temperatures from 320 to 375°C. Although the sensor output at 290°C gradually increased over time independent of CH_4 concentration changes, the sensor output above 320°C, which is close to the complete CH_4 oxidation temperature, changed successively with CH_4 concentration changes within a T_{50}, time to reach 50% of equilibrium signal, of 13 s. Furthermore, the sensor output increased linearly with increasing CH_4 concentration above 320°C, with R^2, the coefficient of determination, exceeding 0.990, confirming that the present sensor exhibits a quantitative response to CH_4 above 320°C.

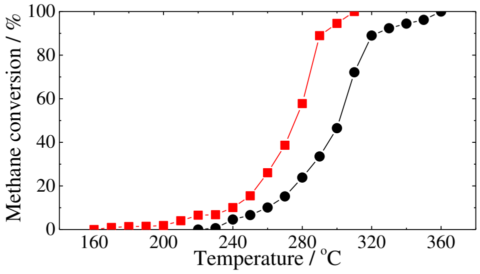

Fig. 2. Temperature dependence of methane conversion for the PdO/GdSiO/AlO (■) and PdO/AlO (●) catalysts

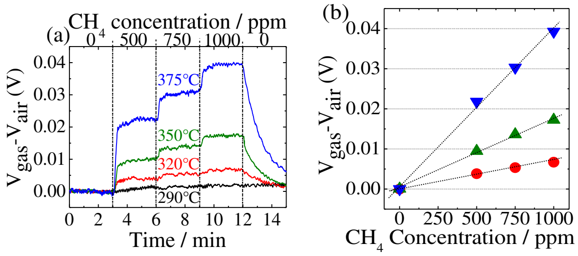

Fig. 3. (a) Response curves at various temperatures and (b) sensor outputs at various methane concentrations for the sensor incorporating the PdO/GdSiO/AlO catalyst at 320°C (●), 350°C (▲) and 375°C (▼)

Conclusion

In summary, a sensor incorporating an 11.3 wt.% PdO/20 wt.% $Gd_{10}Si_6O_{27}$/γ-Al_2O_3 catalyst was developed to achieve low-temperature CH_4 detection. By applying apatite-type $Gd_{10}Si_6O_{27}$, which exhibits oxide ion conductivity, as a promoter, the CH_4 oxidation activity of PdO was successfully improved. Moreover, the sensor incorporating this catalyst showed a quantitative response to CH_4 even at 320°C, which is approximately 100°C lower than the minimum operating temperature of the conventional sensor with the PdO/AlO catalyst.

Acknowledgments

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