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Author(s)	Lee, Wonjoon; Tamura, Shinji; Imanaka, Nobuhito
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Supporting Information

Catalytic Combustion-Type Methane Gas Sensors with Tungsten-doped Apatite-type Gadolinium Silicate

Wonjoon LEE¹, Shinji TAMURA^{1*}, Nobuhito IMANAKA¹

¹*Division of Applied Chemistry, Graduate School of Engineering,
The University Osaka, Osaka 565–0871, Japan*

E-mail: shinji@chem.eng.osaka-u.ac.jp

Composition of promoters measured by XRF.

Table S1 shows the chemical composition of GSW_x ($x = 0.1\text{--}1.0$) promoters measured by XRF analysis. The measured tungsten doping levels agree well with the expected stoichiometric ratios, indicating successful synthesis and effectively incorporation of tungsten.

Table S1. Composition of promoters measured by XRF.

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

Raman peak assignments for the GS and GSW_x ($x = 0.1$ – 1.0) promoters

Table S2 summarizes the Raman peaks observed for the GS and GSW_x ($x = 0.1$ – 1.0) promoters. Each Raman band is assigned to specific vibrational modes of the catalyst components, including: external (translational and librational) motions of Gd ions and SiO₄ units in the low-frequency region below 350 cm⁻¹; internal bending modes in the 350–600 cm⁻¹ range; and stretching modes above 750 cm⁻¹, attributed to Si–O and W–O bonds (WO₄, WO₅, and WO₆ structural units). Relevant literature references supporting these spectral assignments are also provided.

Table S2. Raman peak assignments for the GS and GSW_x ($x = 0.1$ – 1.0) promoters.

GS	Raman shift (cm ⁻¹) of GSW _x					Assigned Mode	References
	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	S1, S3
147	148.9	147.1	149.2	148.1	-	Translations and librations of Gd ions	S1, S3
171.1	168	167	-	-	-	Translations and librations of Gd ions	S1, S2, S4, S5
222.6	221.6	223.4	-	-	-	Translations and librations of SiO ₄	S1, S2, S4
-	-	241.2	242.5	243.3	241.9	Translations and librations of Gd ions	S1, S3, S4
276.7	281.2	281.7	281.5	276.9	-	Translations and librations of Gd ions	S1, S4, S6
309.4	312.7	313.2	312.5	-	-	Translations and librations of Gd ions	S1, S2
344.2	340.6	342.9	-	-	-	Translations and librations of Gd ions and SiO ₄	S1, S2, S6
364.3	366.1	366.4	-	368.7	364.6	Bending modes of Si-O (SiO ₄)	S4, S7
386.1	-	-	-	-	-	Bending modes of Si-O (SiO ₄)	S4, S5, S7
417.5	413.5	403.2	400.1	-	-	Bending modes of Si-O (SiO ₄)	S2, S4, S9
454.1	438.4	438.9	-	-	-	Bending modes of Si-O (SiO ₄)	S7–S9
492.1	485.9	488.8	-	-	-	Bending modes of Si-O (SiO ₄)	S7–S9
547	536	521.5	523.3	519.3	-	Bending modes of Si-O (SiO ₄)	S2, S5, S7–S9
-	739.3	742.2	741.7	-	801.3	Stretching modes of W-O (WO ₆)	S8, S10, S11
-	829.8	830.3	829.4	827.1	-	Stretching modes of W-O (WO ₅)	S6, S11
886	881.9	880.9	879.9	880	-	Stretching modes of Si-O (SiO ₄)	S2, S4, S5
-	-	-	916.4	916.5	921.1	Stretching modes of W-O (WO ₄)	S10, S11
943.9	939.3	-	-	-	-	Stretching modes of Si-O (SiO ₄)	S2, S4, S5

Temperature dependencies of the methane conversion for PdO/GS/AlO and PdO/GSW_x/AlO (*x* = 0.1–1.0)

The methane oxidation activity of the PdO/GS/AlO and PdO/GSW_{*x*}/AlO (*x* = 0.1–1.0) catalysts was evaluated using a conventional fixed-bed flow reactor consisting of a quartz tube with an inner diameter of 10 mm. The feed gas contained 1 vol% methane in air, with a total flow rate of 33.4 mL·min⁻¹, corresponding to a space velocity (SV) of 20,000 L·kg⁻¹·h⁻¹.

Figure S1 presents the methane conversion profiles of PdO/GS/AlO and PdO/GSW_{*x*}/AlO (*x* = 0.1–1.0) catalysts. All samples exhibited catalytic activity toward methane combustion. Compared to the undoped sample, tungsten doping resulted in upward shift in both the onset and complete conversion temperatures. This behavior is attributed to the formation of strong W–O bonds within the catalyst lattice, which suppress the formation and mobility of oxygen vacancies. Consequently, the supply of active oxygen species from the promoter to PdO is hindered, leading to reduced catalytic activity for CH₄ oxidation.

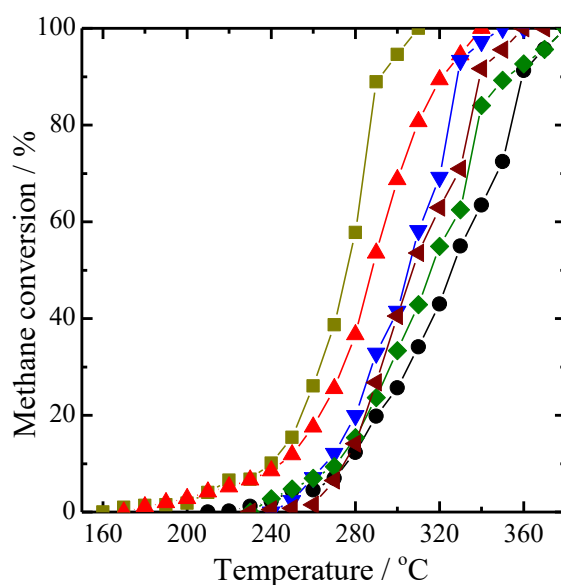


Fig. S1. Temperature dependencies of the methane conversion for PdO/GS/AlO (yellow) and PdO/GSW_{*x*}/AlO (*x* = 0.1 (black), 0.3 (red), 0.5 (blue), 0.7 (green), 1.0 (wine)).

Operating temperature of sensor using PdO/GS/AlO and PdO/GSW_x/AlO ($x = 0.1$ – 1.0) catalysts

Table S3 lists the operating temperatures of methane gas sensors incorporating PdO/GS/AlO and PdO/GSW_{*x*}/AlO ($x = 0.1$ – 1.0) catalysts. Increasing the tungsten doping level up to $x = 0.3$ enabled methane detection at low temperatures, reaching as low as 290 °C. However, further increases in W content led to a rise in the required operating temperature.

Table S3. Operating temperature of sensor using PdO/GS/AlO and PdO/GSW_{*x*}/AlO ($x = 0.1$ – 1.0) catalysts.

Sensor	Operating temperature / °C
PdO/GS/AlO	320
PdO/GSW _{0.1} /AlO	290
PdO/GSW _{0.3} /AlO	290
PdO/GSW _{0.5} /AlO	320
PdO/GSW _{0.7} /AlO	350
PdO/GSW _{1.0} /AlO	350

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