Catalytic methane combustion over novel catalyst based on oxide-ion-conducting lanthanum silicate

Naoyoshi NUNOTANI, Naoki MORIYAMA, Kenji MATSUO and Nobuhito IMANAKA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2–1 Yamadaoka, Suita, Osaka 565–0871, Japan

A novel PdO/La10Si6O27/y-Al2O3 catalyst was developed in order to decompose methane. In this catalyst, we selected the oxide-ion-conducting La10Si6O27 solid with an apatite-type structure as a promoter to facilitate the supply of active oxygen to the PdO activator. For the comparison with PdO/La10Si6O27/y-Al2O3, where La2O3 is a simple rare earth sesquioxide, the catalytic activity of PdO/La10Si6O27/y-Al2O3 was higher than that of PdO/La2O3/y-Al2O3, regardless of their same surface area. Since La10Si6O27 exhibited two orders of magnitude higher conductivity than La2O3, the high oxide-ion-conducting property of La10Si6O27 might facilitate the oxidation of methane by supplying active oxygen from inside the lattice.

Key-words : Methane, Apatite-type, Lanthanum silicate, Catalyst, Oxidation

Methane (CH4) is the major component of natural gas, which is a significant fuel resource. However, methane is the second most predominant greenhouse effect gas after carbon dioxide, because the warming effect of methane is approximately 20 times higher than that of carbon dioxide. In addition, it is reported that the methane emission by fossil fuel usage and production is 20–60% higher than in current global inventories. From the view point of reducing global warming, it is necessary to minimize anthropogenic methane emissions, such as a release of unburned natural gas from the combustor and a leak of natural gas from pipeline.

One effective method to abate methane emission is the employment of catalytic exhaust converters, in which methane is combusted, palladium oxide (PdO) was eagerly studied, because of its highly catalytic oxidation ability. In the previous studies, PdO supported on ceria (CeO2) based systems have been studied widely as a high oxide-ion-conducting solid electrolyte for potential usage in solid oxide fuel cell (SOFC) applications. Since this tunnel is oxide-ion-conducting pathway, La10Si6O27 exhibited high oxide ion conductivity at intermediate temperature range (300–600°C). Also, since La3+ and Si4+ ions are regarded to be suitable for the constitution ions from the view point of their single valence states of trivalent and tetravalent, respectively, La10Si6O27 shows pure oxide ion conductivity without any electronic conduction. For these reasons, an apatite-type La10Si6O27 systems have been widely studied as a high oxide-ion-conducting solid electrolyte for potential usage in solid oxide fuel cell (SOFC) applications. Based on this concept, we prepared the PdO/La10Si6O27/y-Al2O3 catalyst, composed of a PdO activator with high methane catalytic activity, the La10Si6O27 promoter with high oxide-ion-conducting property, and a γ-Al2O3 support with high surface area, and investigated the effect of oxide ion migration on the catalytic activity for methane oxidation.

La10Si6O27 was prepared by a sol–gel method. Stoichiometric La(NO3)3·6H2O and Si(OCH2CH3)4 (Kishida Chemical) were dissolved into a mixture of 75 cm3 ethanol and 1.5 cm3 acetic acid. After stirring for 1 h at room temperature, polyvinyl pyrrolidone (PVP; Wako Pure Chemical Industries) was dissolved in the mixed solution. After the solution was stirred at 80°C for 2 h, the solution was evaporated at 180°C, then preheated at 350°C and calcined at 1000°C for 2 h under flowing air. Commercial γ-Al2O3 (AxSorb AB, Nippon LightMetal) was mechanically dry pulverized using a ball-milling apparatus (Pulversette 7, FRITSCH). La10Si6O27 and γ-Al2O3 were mixed with La10Si6O27...
content adjusted to 20 wt%, and wet ball milled in ethanol. The mixture was then heated at 500°C for 4 h in air to obtain La10Si6O27/γ-Al2O3. A palladium supported on catalyst was prepared by the impregnation of Pd(NO2)2(NH3)2 solution (Tanaka Kikinzoku Kogyo) into the La10Si6O27/γ-Al2O3 sample. Then, the catalyst was dried at 80°C for 12 h and calcined at 500°C for 4 h. The amount of PdO was adjusted to 11.3 wt%. Hereafter, we denoted the 11.3 wt% PdO/20 wt% La10Si6O27/γ-Al2O3 as PdO/La10Si6O27/γ-Al2O3. For comparison, 11.3 wt% PdO/20 wt% La10Si6O27/γ-Al2O3 (PdO/La10Si6O27/γ-Al2O3) was also synthesized by the same method without using (OC)2H4Al.

The samples were characterized by X-ray powder diffraction (XRD; SmartLab, Rigaku) with Cu-Kα radiation (40 kV and 30 mA). X-ray fluorescence (XRF; ZSX100e, Rigaku) was used to determine the compositions of the catalysts. Brunauer–Emmett–Teller (BET) specific surface area was measured by nitrogen adsorption at −196°C (Tristar 3000, Shimadzu). For the conductivity measurement, La10Si6O27 and La2O3 solids were pressed into a pellet using uniaxial pressing, and then, the pellets were sintered at 1400°C for 12 h in the air flow. After the sintering process, AC conductivity of the pellets was measured using a complex impedance method (1260 impedance analyzer, Solartron) in the frequency range between 5 Hz and 13 MHz in air.

The methane oxidation activity was carried out in a conventional fixed-bed flow reactor consisting of a quartz glass tube (diameter = 10 mm). The feed gas was composed of 1 vol% methane-air, and a rate was 33.4 cm³·min⁻¹ over 0.1 g of catalyst (space velocity = 20 m³·kg⁻¹·h⁻¹). Before the catalytic activity experiment, the catalysts were pre-treated at 200°C for 2 h under argon flow (20 cm³·min⁻¹) to remove water adsorbed on the surface of the catalyst. The catalytic activity was evaluated in terms of methane conversion. The gas composition after the reaction was analyzed by using a gas chromatograph with thermal conductivity detection (GC-8AIT, Shimadzu).

From the XRD measurement of the La10Si6O27 promoter, the single phase of apatite-type structure was confirmed. Figure 1 shows AC conductivity of La10Si6O27, for comparison with the result for a simple rare earth sesquioxide of La2O3. AC conductivity of La10Si6O27 (σₑ at 0°C = 1.0 × 10⁻⁴ S·cm⁻¹) was almost the same value as the previous study (σₑ at 0°C ~ 3.1 × 10⁻⁴ S·cm⁻¹) [17]. In addition, the conductivities of La10Si6O27 were two orders of magnitude higher than those of La2O3 for each temperature, because apatite-type structure possesses the oxide-ion-conducting pathway.

For the PdO/La10Si6O27/γ-Al2O3 and PdO/La2O3/γ-Al2O3 catalysts, the compositions measured by XRF (11.4 wt% PdO/20 wt% La2O3/γ-Al2O3, 11.9 wt% La2O3/γ-Al2O3) were in good agreement with their stoichiometric values. The BET surface area of PdO/La10Si6O27/γ-Al2O3 (133 m²·g⁻¹) was comparable with that of PdO/La2O3/γ-Al2O3 (133 m²·g⁻¹), and these values were lower than that of γ-Al2O3 (274 m²·g⁻¹). The decrease of the surface area indicates that the PdO and La10Si6O27 or La2O3 particles are supported in the pores of the γ-Al2O3 support. XRD patterns of the prepared catalysts are shown in Fig. 2. The pattern of PdO/La10Si6O27/γ-Al2O3 indicates the formation of PdO, an apatite-type phase, and γ-Al2O3, and the peaks for PdO/La2O3/γ-Al2O3 were indexed by PdO, La2O3, and γ-Al2O3. For both catalysts, neither crystalline impurities nor metallic palladium was observed. In addition, the crystalline sizes of PdO were almost the same values (PdO/La10Si6O27/γ-Al2O3: 6.4 nm, PdO/La2O3/γ-Al2O3: 6.7 nm), calculated by Scherrer equation.

Figure 3 shows the temperature dependencies of methane conversion in the PdO/La10Si6O27/γ-Al2O3 and PdO/La2O3/γ-Al2O3 catalysts. Here, methane was fully oxidized to carbon dioxide and steam, and neither carbon monoxide nor methane-derived byproducts were detected by gas chromatography-mass spectrometry. The methane conversion activity for PdO/La10Si6O27/γ-Al2O3 was obviously higher than the case for PdO/La2O3/γ-Al2O3. In other words, for PdO/La10Si6O27/γ-Al2O3, methane was completely oxidized at 390°C, and this value is ca. 50°C lower than that for PdO/La2O3/γ-Al2O3 (440°C). This result indicates that the La10Si6O27 promoter affected the catalytic activity. Although there is a possibility that La10Si6O27 worked as a catalyst for methane oxidation, the role of La10Si6O27 was not the catalyst but the promoter due to the fact that the La10Si6O27/γ-Al2O3.
\( \gamma-\text{Al}_2\text{O}_3 \) sample without PdO did not exhibit the catalytic activity, as shown in Fig. 3.

Here, we describe the effect of the promoter on the catalytic activity. According to the previous studies, the catalytic methane oxidation on PdO is easier to proceed compared to metallic Pd, while this process is accompanied by the reduction of PdO to Pd.\(^{21}\) In general, re-oxidation of Pd metal is proceeded by two steps of the adsorption of gaseous oxygen onto Pd [Eq. (1)] and the reaction between Pd and adsorbed oxygen [Eq. (2)].\(^{22-25}\)

\[
\begin{align*}
\frac{1}{2} \text{O}_2(\text{gas}) & \rightarrow \text{O}_{\text{ad}}(\text{Pd}) \\
\text{Pd}^0 + \text{O}_{\text{ad}}(\text{Pd}) & \rightarrow \text{PdO}
\end{align*}
\]

where \( \text{O}_{\text{ad}}(\text{Pd}) \) is adsorbed oxygen on Pd. Furthermore, by using oxide-ion-conducting solid electrolytes as a promoter, it is considered that an additional re-oxidation mechanism proceeds involved with the oxide ion migration, as shown in Eqs. (3) and (4). Since oxide ion is easy to conduct inside the lattice, it would oxidize Pd metal to PdO:

\[
\text{Pd}^0 + \text{O}^2- \rightarrow \text{PdO} + 2\text{e}^-
\]

The generated electron migrates through the catalyst, and then, reduces adsorbed oxygen on the promoter to oxide ion near the catalyst-promoter-gas interface:

\[
2\text{e}^- + \text{O}_{\text{ad}}(\text{promoter}) \rightarrow \text{O}^2-
\]

where \( \text{O}_{\text{ad}}(\text{promoter}) \) is adsorbed oxygen on the promoter. The oxide ion also conducts inside the lattice, and combines with the oxygen vacancy, generated by Eq. (3). It is most likely that this scheme facilitates the catalytic activity, because PdO/La\(_{10}\)Si\(_6\)O\(_{27}\)/\( \gamma-\text{Al}_2\text{O}_3 \) exhibited the higher catalytic activity compared with PdO/La\(_9\)Si\(_8\)O\(_{27}\)/\( \gamma-\text{Al}_2\text{O}_3 \), where the conductivity of La\(_{10}\)Si\(_6\)O\(_{27}\) was two orders of magnitude higher than that of La\(_9\)Si\(_8\)O\(_{27}\).

In summary, a novel catalyst composed of PdO/La\(_{10}\)Si\(_6\)O\(_{27}\)/\( \gamma-\text{Al}_2\text{O}_3 \) was developed for methane combustion. By selecting the oxide-ion-conducting La\(_{10}\)Si\(_6\)O\(_{27}\) solid as a promoter, the catalytic activity was enhanced compared to the La\(_9\)Si\(_8\)O\(_{27}\) case because the supply of oxide ions from La\(_9\)Si\(_8\)O\(_{27}\) might facilitate the re-oxidation of Pd metal, generated in the process of methane oxidation. The complete methane combustion for PdO/La\(_9\)Si\(_8\)O\(_{27}\)/\( \gamma-\text{Al}_2\text{O}_3 \) was achieved at the temperature of 390°C, which is ca. 50°C lower than that for PdO/La\(_9\)Si\(_8\)O\(_{27}\)/\( \gamma-\text{Al}_2\text{O}_3 \).

References


