Methane Combustion over Lanthanoid Perovskite Catalysts

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Abstract: Methane combustion over perovskite catalysts was investigated using a fixed-bed reactor at 1 bar. Co, Mn, Fe, and Ni were used as the B-site of the perovskite catalysts (ABO₃) and La was used as the A-site. The effect of the calcination temperature on methane combustion and the structure of the perovskite were also investigated. Using XRD, surface area measurements, and O₂-TPD, the effects of the perovskite structure, oxygen species adsorbed, and surface area on methane combustion were all examined. The formation of a perovskite structure was affected by the calcination temperature. A catalyst desorbing oxygen at a lower temperature was better for methane combustion, whereas an oxygen species desorbing at a lower temperature was found to be responsible for methane combustion.

Keywords: methane combustion; perovskite catalyst; calcinations temperature; oxygen species

Introduction

The catalytic combustion of fuels has certain advantages including lower pollutant emission and higher energy efficiency. Recently, regulations on the exhaust of vehicles and burners have become so strict that research on the catalytic combustion of fuels has become more important. In particular, NOx, produced by the oxidation of nitrogen in air above 1600 K, is one of the main air pollutants. However, with a catalyst, it is possible to achieve the complete combustion of fuels below 1200 K, so that no NOx is emitted [1].

Methane is a chemically stable compound, therefore, it is hard to combust it completely. As such, any unburned methane becomes a source of air pollution. In general, it is known that the main source of air pollution is carbon dioxide, however, the extent of the greenhouse effect due to methane is about 21 times larger than that of carbon dioxide [2]. Therefore, owing to the increased use of methane, it is necessary to develop catalysts that can decrease the emission of NOx and unburned methane.

Palladium is known as an active noble metal for methane combustion [3-8]. Anderson et al. previously reported that Pd and Pt are good catalysts for methane combustion [9]. Drozdov [10] and Schwartz [11] also reported that Pd is a good catalyst for methane combustion, while Pt is a good catalyst for the combustion of C₃ hydrocarbons. Firth [12] examined the catalytic activities of noble metals (Pd, Pt, Ir, Rh) for methane combustion at 400 °C, and reported on the order of the catalytic activities as follows: Pd > Rh > Ir > Pt. In addition, he reported that the reaction activity increased with the amount of oxygen adsorbed. Armor [13] compared the catalytic activities of PdO/Al₂O₃ and Pd ion-exchanged ZSM-5 catalysts for methane combustion. He reported that the Pd ion-exchanged ZSM-5 catalyst exhibits a higher activity than PdO/Al₂O₃ and proposed that the oxygen adsorbed on the surface of the zeolite is responsible for the higher activity. However, these noble metal catalysts have some disadvantages: they are expensive and easily deactivated at an elevated temperature. Accordingly, current research is focusing on the development of catalysts that are cheap, stable at a high temperature and active for methane combustion [14]. The perovskite (ABO₃) is just the material that meets these needs. However, the perovskite catalyst has a disadvantage of small surface area.

The perovskite materials are represented by a general formula of ABO₃, in which A-site can be rare earth, alkaline earth, and alkali metals and the B-site can be 3d, 4d, and 5d transitional metals [15]. There are many
papers on hydrocarbon combustion with perovskite catalysts, however the catalytic activities are lower than noble metal catalysts [16, 17]. This lower activity may be stemmed from its lower surface area. There were many trials to get a high surface area perovskite catalyst. Teraoka [18] could prepare a perovskite catalyst whose surface area was higher than 10 m²/g by the addition of citric acid or maleic acid in the preparation process.

Klvan [19] reported that a perovskite catalyst whose A-site or B-site is partially substituted exhibits as high methane combustion activity as noble metals. Marchetti [20] also reported that by a partial substitution of A-site by an element having lower oxidation state the catalytic activity is increased by the formation of anion vacancies. Saracco [21] reported two kinds of oxygen species desorbing from the perovskite: desorbing around 300-500 °C and desorbing at higher temperature. He also proposed that by partial substitution of A-site the anion vacancies are easily generated and the anion vacancies make oxygen easy to adsorb and desorb, consequently, it increases the catalytic activity. Ferri [22] proposed that oxygen species desorbing at a lower temperature was from anion vacancies and oxygen species desorbing at a higher temperature was from a lattice. In addition, he reported that methane combustion activity is directly related to the oxygen species desorbing at a lower temperature. Yamazoo [23] also reported that partial substitution of A-site increased the methane combustion activity by increasing the amount of oxygen species desorbing at a lower temperature.

The perovskite catalysts were prepared by a citrate method, and the effect of calcination temperature on the structure of perovskite catalyst was examined. In addition, we investigated characteristics of the catalysts with changing B-sites.

### Experimental

The catalysts were prepared by the citrate method using the following reagents: La(NO₃)₃·6H₂O (Junsei), Co(NO₃)₂·6H₂O (Duskan), Mn(NO₃)₂·6H₂O (Junsei), Ce(NO₃)₃ (Junsei), Ag(NO₃)₃ (Inusinho), Ca(NO₃)₂·4H₂O (Duskan), citric acid (Shinyo), Sr(NO₃)₂ (Jusei), and Ba(NO₃)₂ (Junsei). The catalysts were prepared as follows. First, the metal nitrates were individually dissolved with distilled water, mixed, and stirred thoroughly for 30 minutes. Then, citric acid corresponding to the amounts of the mixed nitrates was dissolved in distilled water, then this solution mixed with the nitrate solutions prepared previously. Next, the solution was heated at around 60-80 °C for 2 hours with stirring. Then, the gelled solution was dried in a drying oven for 12 hours. The dried catalyst was crushed, and then calcined in flowing air for 3 hours at various temperatures as described in Table 1. The prepared catalysts were then crushed, sieved through a 80–100 mesh, and used to test their activity. The names of the prepared catalysts are listed in Table 1.

A fixed-bed quartz tube reactor was used. An ice bath and moisture trap was placed at the end of the reactor to remove any water produced. The reactants and products were analyzed with an on-line GC (Youngin 680D). The amount of catalyst used for the reaction was 0.1 g and the total flow rate of the reactants was 40 ml/min (CH₄, 2 vol%; O₂, 21%; He, balance). All the combustion reactions were carried out at 1 bar. For an analysis of the CH₄, O₂, and CO₂, a carbosphere column material was used and the carrier gas was He.

The catalyst surface areas were measured with a Pulse Chemisorb 2700 (Micromeritics). The composition and structure of the perovskite catalysts were tested with an XRD (Shimazu). The characteristics of the oxygen adsorption and desorption on the catalysts were tested with an O₂-TPD experiment using TCD detector. The procedure for the O₂-TPD experiment was as follows. In order to pre-treat the catalyst, 0.05 g of the catalyst was loaded in a quartz tube, heated from room temperature to 300 °C at a rate of 10 °C/min with a flow of 20 ml He/min, and then held at 300 °C for 2 hours. Next, under a flow of a mixed gas (10 vol% O₂ and 90% He) at a rate of 40 ml/ min, the catalyst was cooled down to 50 °C and held at that temperature for 1 hour to adsorb O₂. Thereafter, the catalyst was heated up to 900 °C at a rate of 10 °C/min.

**Table 1. Catalysts prepared by citrate method**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination Temperature (°C)</th>
<th>Name of Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO₃</td>
<td>600</td>
<td>LC-6</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>700</td>
<td>LC-7</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>800</td>
<td>LC-8</td>
</tr>
<tr>
<td>LaMnO₃</td>
<td>700</td>
<td>LM-7</td>
</tr>
<tr>
<td>LaNiO₃</td>
<td>700</td>
<td>LN-7</td>
</tr>
<tr>
<td>LaFeO₃</td>
<td>700</td>
<td>LF-7</td>
</tr>
<tr>
<td>La₄Ce₀.₁MnO₃</td>
<td>700</td>
<td>LCM-7</td>
</tr>
<tr>
<td>La₄Ce₀.₁MnO₃</td>
<td>800</td>
<td>LCM-8</td>
</tr>
<tr>
<td>La₄Ce₀.₁MnO₃</td>
<td>900</td>
<td>LCM-9</td>
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<tr>
<td>La₄Sr₀.₁MnO₃</td>
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<td>LSM-7</td>
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<tr>
<td>La₄Sr₀.₁MnO₃</td>
<td>800</td>
<td>LSM-8</td>
</tr>
<tr>
<td>La₄Sr₀.₁MnO₃</td>
<td>900</td>
<td>LSM-9</td>
</tr>
<tr>
<td>La₄Ba₀.₁MnO₃</td>
<td>700</td>
<td>LBM-7</td>
</tr>
<tr>
<td>La₄Ag₀.₁MnO₃</td>
<td>700</td>
<td>LAM-7</td>
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</table>
Results and Discussion

Effect of calcination temperature on catalyst structure and methane conversion

The structure and surface area of a perovskite catalyst are affected by its calcination temperature. The methane combustion reaction was performed at 600 °C with a LaCoO$_3$ catalyst that had been calcined at 600, 700, and 800 °C to determine the effect of the calcination temperature on the methane conversion and identify the optimum calcination temperature. Figure 1 shows the methane conversion as a function of the calcination temperature. The methane conversions were 90, 60, and 40% for the LC-7 (LaCoO$_3$, calcined at 700 °C), LC-6 (LaCoO$_3$, calcined at 600 °C), and LC-8 (LaCoO$_3$, calcined at 800 °C) catalysts, respectively. The full names and calcination conditions of the catalysts are listed in Table 1. As shown in Figure 1, there was no decrease in the methane conversion relative to time for 24 hours. Plus, the catalyst calcined at 700 °C showed about a 90% methane conversion.

The surface areas of the catalysts calcined at several temperatures were measured using surface area measuring equipment and are depicted in Figure 2. As expected, the surface areas of the catalysts decreased with the calcination temperature. When comparing the surface areas of the catalysts before and after the reaction, there was no significant change in the surface area. This means that perovskite catalysts are more resistant to sintering than noble metal catalysts, which usually sinter above 500 °C.

Based on the surface area results in Figure 2, it is impossible to explain why the highest methane conversion was with the catalyst calcined at 700 °C in Figure 1. Therefore, the crystallinity of the perovskite catalysts was examined by XRD when changing the calcination temperature, and the XRD patterns are presented in Figure 3. The unique peaks of lanthanoid perovskite appeared at 22°, 33°, 41°, 47°, and 58°, thereby confirming the formation of a perovskite crystalline [24]. Furthermore, the crystallinity of the catalysts increased with the calci
nation temperature.

In summary, at all three calcination temperatures, a perovskite crystalline was formed, and the surface areas were inversely proportional to the calcination temperature. However, the highest methane conversion was obtained with a catalyst calcined at 700 °C. To investigate this mismatch between the methane conversion and the surface area, an O₂-TPD experiment was performed and the results are presented in Figure 4. For the LC-6 catalyst, there was no O₂ desorption peak observed within the experimental range. However, the LC-7 catalyst showed a large oxygen desorption peak around 350–550 °C, and for the LC-8 catalyst, oxygen desorption started around 400 °C and showed a sharp peak around 680 °C. From this TPD result, it would appear that the low methane conversion of the catalysts calcined at 600 °C was owing to their low oxygen adsorption. When comparing the TPD results of the LC-7 and LC-8 catalysts, the LC-8 catalyst showed an oxygen desorption peak at a higher temperature, whereas the LC-7 catalyst showed a large oxygen desorption peak at a lower temperature. From these results, it can be inferred that the oxygen desorbing at a lower temperature is responsible for the methane conversion. Ferri [22] reported that an oxygen species desorbing at a lower temperature from a LaCoO₃ perovskite catalyst is responsible for methane combustion. Gunasekaran [25] also reported that catalysts prepared using the same method and with the same composition can reveal different activities for methane combustion depending on their calcination temperature.

He also proposed that oxygen desorption peaks shift to a higher temperature with an increase in the calcination temperature.

When combining the results obtained from the XRD, surface area measurements, and O₂-TPD experiment, it would seem that those catalysts that can easily adsorb and desorb oxygen at a lower temperature are reactive catalysts for methane combustion.

**Effect of B-Site Change on Catalytic Activity**

The general expression for a perovskite is ABO₃. The change in the catalytic activity relative to a B-site change of the catalysts was investigated. In this study, the B-site materials used were Co, Mn, Fe, and Ni. The methane combustion reaction was carried out with perovskite catalysts whose B-site had been exchanged and that had been calcined at 700 °C, and the result is shown in Figure 5. Complete methane combustion was obtained with the LM-7 catalyst at 600 °C, about 90% methane conversion.
was obtained with the LF-7 catalyst, and about 85–90% methane conversions were obtained with the LC-7 and LN-7 catalysts. The catalytic activities remained constant for 24 hours.

The surface areas of the catalysts whose B-sites had been exchanged are shown in Figure 6. The surface area of the LM-7 catalyst, which exhibited the highest catalytic activity, was 25 m²/g, whereas the surface area of LN-7 was 17 m²/g. The catalytic activities of the three catalysts, except for LN-7, were proportional to their surface areas.

Using XRD, the crystallinity of the catalysts was examined, as shown in Figure 7. The LF-7 and LN-7 catalysts exhibited the unique perovskite peaks, while the LN-7 catalyst, which showed the lowest catalytic activity, exhibited almost no perovskite crystallinity. Based on this result, it would appear that the highest catalytic activity of the LM-7 catalyst stemmed from both its large surface area and well-formed perovskite crystallinity.

In order to examine the effect of oxygen adsorption and desorption on the catalytic activity, an O₂-TPD experiment was carried out with the LM-7 and LF-7 catalysts, which showed a definite perovskite structure. The results are depicted in Figure 8. For the LM-7 catalyst, oxygen started to desorb from 300 °C, which then continued with a large amount of oxygen to around 700 °C. When compared with Figure 4, the amount of desorbing oxygen with the LM-7 catalyst was larger than that with the LC-7 catalyst per unit mass. Seiyama [26] reported that, unlike a LaCoO₃ catalyst, a LaMnO₃ catalyst holds excess oxygen in its lattice. Therefore, the LM-7 catalyst, which desorbs a large amount of oxygen at a lower temperature, is a good catalyst for methane combustion. In contrast, the LF-7 catalyst only showed one small peak around 700 °C. Based on these results, it can be concluded that the methane desorbing at a lower temperature is responsible for methane combustion.

**Conclusions**

The formation of a perovskite structure was affected by the calcination temperature. For an ABO₃-type perovskite, its crystalline was formed at a calcination temperature of 700 °C. A catalyst that can adsorb and desorb oxygen at a lower temperature is better for methane combustion.

Mn was found to be the best metal for the B-site, and complete methane combustion was achieved at 600 °C. This was due to a large surface area, well-formed perovskite crystalline, and large amount of oxygen desorption at a lower temperature.

From an O₂-TPD experiment, it was found that a catalyst that desorbed oxygen at a lower temperature exhibited better activity for methane combustion. Accordingly, an oxygen species affecting methane combustion is not one that desorbs at higher temperature, but rather
one that desorbs at a lower temperature.

Acknowledgement

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References