

Catalytic Combustion of Methane over Perovskite-Type Oxides

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(Manuscript received on March 14, 2000)

Methane combustion over perovskite-type oxides prepared using the malic acid method was investigated. To enhance the catalytic activity, the perovskite oxides were modified by the substitution of metal into their A or B site. In addition, the reaction conditions, such as the temperature, space velocity, and partial pressure of the methane were varied to understand their effect on the catalytic performance. With the LaCoO₃-type catalyst, the partial substitution of Sr or Ba into site A enhanced the catalytic activity in the methane combustion. With the LaBO₃(B=Co, Fe, Mn, Cu)-type catalyst, the catalytic activities were exhibited in the order of Co>Fe≅Mn>Cu. Furthermore, the partial substitution of Co into site B enhanced the catalytic activity, whereas an excess amount of Co decreased the activity. The surface area and catalytic activity of the perovskite catalysts prepared using the malic acid method showed higher values than those prepared using the solid reaction method. The catalytic activity was enhanced with decreased methane concentration and with a decrease in the space velocity.

Key words : Catalytic Combustion of Methane, Perovskite-Type Oxides, Malic Acid Method, Substitution of Sr, Ba or Co

1. Introduction

Because of its potential economic and environmental advantages over other hydrocarbons and its relative abundance, natural gas has been widely used as a fuel for electrical utilities and has attracted considerable attention as an alternative fuel for motor vehicles¹⁾. However, the related methane emission is a potential environmental problem as it is known as to contribute to the greenhouse effect. Most of the attention on global warming has been focussed on the presence of carbon dioxide in the atmosphere, however, methane is also a significant contributor. Although the volume of methane emission is much smaller than that of carbon dioxide, it is about 20 times more potent than carbon dioxide as a greenhouse gas²⁾.

Catalytic combustion is considered to be an effective approach for controlling the emission of natural gas. High combustion efficiencies can be

achieved with temperature conditions and concentrations that are much lower than those normally required for a stable homogeneous gas phase reaction to proceed. Complete oxidation at a low combustion temperature results in minimum thermal-NO_x formation and better fuel efficiency. As a result, it would appear to solve the environmental problem.

The noble metals(Pt, Pd, Rh) and metal oxides (oxides of Ni, Cu, Co, Cr, Mn) supported on alumina and silica have been intensively studied related to the catalytic combustion of hydrocarbons^{3~7)}. Plus, transition metal-mixed oxide catalysts based on a perovskite-type structure are now being investigated in this field, in relation to their thermal stability and activity in a catalytic combustion reaction^{8,9)}.

Perovskite-type oxides, which are structurally similar to the mineral of that name (CaTiO₃), have long been studied because of their technologically

important characteristics. In 1971, cobaltate perovskites were suggested as substitutes for noble metals as an automotive exhaust catalyst¹⁰.

In the present work, several kinds of perovskite-type oxides were prepared using the malic acid method and their properties characterized. In addition, their catalytic activity on methane combustion in the presence of oxygen was also examined along with the effect of certain reaction conditions, such as reaction temperature and contact time.

2. Experimental

The preparation method of the perovskite-type oxides is outlined in a previous paper¹¹. Malic acid was added to a mixed aqueous solution of metal nitrates in the desired proportion so that the molar ratio of malic acid to the total metal cations was unity. The pH of the mixed aqueous solution was controlled at 4.0 by the addition of ammonia water. The solution was then evaporated to dryness with stirring, and further dried at 150°C. The precursor was ground and then calcined in air at 200°C for 30 min, 350°C for 30 min, and 600°C for 12 h. The calcination temperature was determined based on the result of a thermal analysis of the precursors. In addition, the solid state reaction method was also used as previously reported¹². The metal oxides were dried at 120°C for 2 h and mixed with metal salt. The mixture was ground in an agate mortar and then calcined at 1050°C for 12 h.

The reaction tests were carried out in a continuous flow fixed-bed reactor. The reactor was a quartz glass tube, 1cm in diameter and 24cm long, mounted in a tubular furnace. A K-type thermocouple was in contact with the catalyst bed. The reaction was carried out within a temperature range of 200~800°C and the flow-rate of the feed was 100cm³/min (gas hourly space velocity GHSV=30,000hr⁻¹) controlled by a mass flow meter/controller (Tylan). The reaction gases CH₄ (4.6%) and O₂ (14.7%), with He as the balance, were used. The outlet gases were analyzed by gas chromatography (SRI 8610B) on a Hysep Dip column.

The methane conversion (χ) was calculated

based on the following equation,

$$\chi (\%) = (1 - A/A_0) \times 100$$

where A is the methane intensity after the reaction and A₀ is initial methane intensity.

The crystal structures of the prepared oxides were examined by powder X-ray diffraction (XRD) with Cu K α radiation (Rigaku Co. Model DMX) and the BET surface area was measured using a BET surface area measuring apparatus (Quanta Chrome Surface Area Analyzer). In addition, Temperature Programmed Reduction (TPR) was carried out using a TCD type detector cell.

3. Results and Discussion

3.1. Characterization of Catalysts

A thermogravimetric analysis of the perovskite-type oxide precursor was carried out to determine the calcination temperature. In addition, the provision of a sufficient reaction time for the formation of the perovskite-type structure was important at each calcination step. From previous results¹³, the precursor was calcined at 200°C for 0.5 h, at 350°C for 0.5 h, and at 600°C for 12 h.

The crystal structures of the prepared oxides were analysed by XRD (shown in Fig. 1). The XRD patterns showed a large peak at 33° which confirmed the formation of the perovskite crystalline phase¹⁴. In addition, even after reactions at high temperatures the catalysts still exhibited a perovskite-type structure.

The surface area of the perovskite oxides was measured by a BET measuring apparatus. Table 1 shows the specific surface areas of the catalysts produced by the preparation methods. While only small surface areas were obtained, less than 1 m²/g, in the catalysts prepared using the solid state reaction method, large surface areas, more than 10 m²/g, were obtained in the catalysts prepared using the malic acid method. Accordingly, it would appear that the latter is calcinated at a lower temperature than the former because malic acid facilitates the complex with the transition metal which then stabilizes the perovskite oxide obtained by the complex at a low temperature.

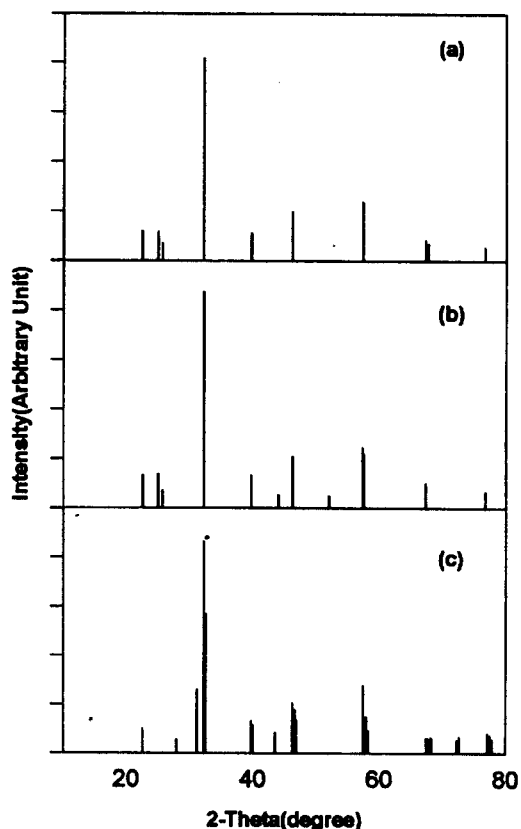


Fig. 1. XRD patterns of perovskite oxides: a) $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ (before reaction), $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ (after reaction), c) $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ (solid state reaction method).

3.2. Effect of Substitution of Metal Ion Into Site A

Fig. 2 shows the effect of the substitution of a metal ion into site A of LaFeO_3 on the methane conversion. The methane conversion increased with an increasing temperature and in the presence of the catalyst, the T_{50} , the temperature at which the conversion reached 50%, decreased dramatically when compared to the absence of the catalyst. In addition, the methane combustion was initiated at about 350°C and in the presence of the catalyst the complete methane conversion was obtained at $600\sim 700^\circ\text{C}$. The substitution of Sr or Ba into site A of LaFeO_3 also increased the methane conversion, however the substitution of Ce produced no effect.

The general formula of perovskites is ABO_3 . Their crystal structure is relatively simple. The B ions can be catalytically active $3d$, $4d$, or $5d$ transition metal ions which occupy an octahedron. The A ions, which fit into dodecahedral interstices, can be large rare-earth, alkaline-earth, alkali or large ions. Even in a single active metal B center, there is still the freedom to vary its valence and many physical properties based on the choices of the modifying A ion. Voorhoeve et al.¹⁵⁾ introduced the term suprafacial and intrafacial catalysis in order to characterize the behavior processes of a series of perovskite-type oxide catalysts. Suprafacial processes are considered to be low-

Table 1. Surface Areas of Various Perovskite Catalysts

Catalyst	Preparation method	Calcining conditions	Specific surface area(m^2/g)
LaFeO_3	Malic acid		
$\text{La}_{0.6}\text{Ba}_{0.4}\text{FeO}_3$	Malic acid	600°C , 12 h	9.9
$\text{La}_{0.6}\text{Ce}_{0.4}\text{FeO}_3$	Malic acid	600°C , 12 h	14.8
$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$	Malic acid	600°C , 12 h	8.0
$\text{La}_{0.6}\text{Sr}_{0.1}\text{FeO}_3$	Malic acid	600°C , 12 h	13.3
$\text{La}_{0.6}\text{Sr}_{0.2}\text{FeO}_3$	Malic acid	600°C , 12 h	16.8
LaMnO_3	Malic acid	600°C , 12 h	14.5
LaCoO_3	Malic acid	600°C , 12 h	10.9
LaCuO_3	Malic acid	600°C , 12 h	13.5
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_3$	Malic acid	600°C , 12 h	6.8
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Co}_{0.2}\text{O}_3$	Malic acid	600°C , 12 h	12.7
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Co}_{0.4}\text{O}_3$	Malic acid	600°C , 12 h	11.8
LaFeO_3	Solid state rxn	600°C , 12 h	5.8
$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$	Solid state rxn	1100°C , 12 h	0.7
		1100°C , 12 h	0.5

temperature processes proceeding through the reactions of adsorbed oxygen (O_{ads}). Conversely, intrafacial or high-temperature processes involve the removal and incorporation of lattice oxygen (O_{lat}). The results of kinetic studies also suggest that the oxidation of methane is a parallel reaction of adsorbed and lattice oxygen^{16,17}. However, recently, many studies have shown that lattice oxygen may be responsible for the combustion of methane¹⁸⁻²⁰. Omata et al.¹⁹ reported that two kinds of lattice oxygen exist in perovskite oxides and the lattice oxygen that is reduced at a low temperature plays an important role in methane combustion. Hong et al.²¹ reported that the substitution of a metal ion into a site of $LaCoO_3$ modifies the lattice oxygen property.

It is understandable that the lattice oxygen in a perovskite-type oxide is important in the methane combustion rate because it is believed that these lattice oxygens are not only strongly bounded to metal but also reversible oxygen species which are involved in the reduction of oxygen by freely moving within lattice metal oxides. It is also suggested that the substitution of Ba or Sr into site A produces reversible lattice oxygen thereby increasing the activity in the methane combustion reaction.

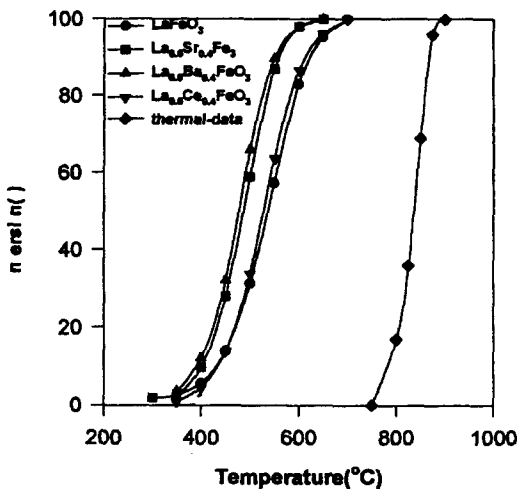


Fig. 2. Catalytic activity in methane combustion with various perovskite catalysts: $CH_4=1$ vol%, $O_2=4$ vol%, $GHSV=30000$ hr^{-1} .

Fig. 3 shows the TPR results of various perovskite oxides. $LaFeO_3$ showed two kinds of

reduction peaks at $450^\circ C$ and $600^\circ C$, respectively. With the substitution of Sr or Ba, the peak size increased at a low temperature. This result suggests that the substitution of Sr or Ba facilitates the increase of reversible lattice oxygen which then increases the catalytic activity in the methane combustion.

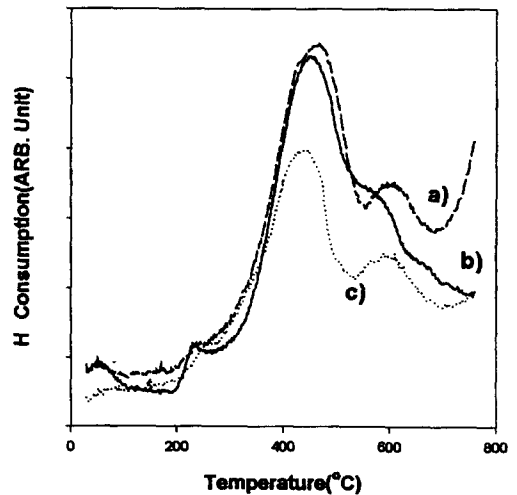


Fig. 3. TPR profiles measured for various perovskite-type oxides calcined at $600^\circ C$ for 12 hs (heating rate = 10 K/min, gas mixture = 7.5% H_2/N_2): a) $La_{0.6}Sr_{0.4}FeO_3$, b) $La_{0.6}Ba_{0.4}FeO_3$, c) $LaFeO_3$.

Fig. 4 shows the effect of the substitution ratio of Sr into site A on the methane combustion. The substitution of Sr into site A decreased the light-off temperature as the substitution ratio increased. However, the catalytic activity showed a maximum value at $x=0.4$ and the light-off temperature decreased above $x=0.4$.

In $La_{1-x}Sr_xCoO_3$, oxygen vacancies compensate for the rising Sr content above $x=0.4$ ²². Obayashi et al. reported that $LaNiO_3$ also promotes the removal of lattice oxygens in the presence of oxygen at temperatures higher than $300^\circ C$ ²³. It is well known that oxygen vacancies are important in an intrafacial catalysis like methane combustion¹⁵. Accordingly, oxygen vacancies resulting from the removal of lattice oxygen are to be expected. Therefore, oxygen vacancies also appear to have an important effect on the catalytic activity in methane combustion.

As the substitution ratio of Sr increased, the

oxygen vacancies increased which then enhanced the catalytic activity by supplying lattice oxygen for the methane combustion reaction. However, with a substitution ratio of $x=0.5$, the light-off temperature increased to a higher temperature. As the substitution ratio of Sr increased, the Sr amount in the lattice also increased. However, above the solubility limit, the excess Sr present on the surface of the perovskite oxides only deteriorated the catalytic performance by prohibiting the adsorption of oxygen on the surface.

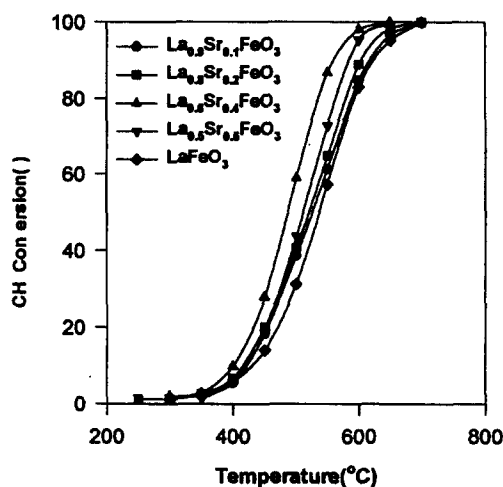


Fig. 4. Catalytic activity in methane combustion with various $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ type perovskite catalysts: $\text{CH}_4=1$ vol%, $\text{O}_2=4$ vol%, $\text{GHSV}=30000$ hr^{-1} .

3.3. Effect of Substitution of Metal Ion Into Site B

Fig. 5 shows the effect of the substitution of a metal ion into site B on the methane combustion reaction. As shown, the substitution of Co into site B resulted in a higher activity than the other metal ions substituted in the following order $\text{Co} > \text{Fe} \approx \text{Mn} > \text{Cu}$.

It is well known that the catalytic activity of perovskite-type oxides depends on the transition metal of site B²⁴. Voorhoeve et al.¹⁵ reported that the substitution of Co into site B showed a higher activity with CO oxidation compared to the substitution of Mn, Fe, Cr, and Ni. In addition, Yamazoe et al.²⁵ reported that Co-based and Mn-based perovskite oxides showed a higher

activity than an Fe-based oxide in a gas phase oxidation reaction. In this study, the catalytic activity of the Co-based perovskite showed the highest activity plus the order of activity was also almost the same as in other oxidation reaction studies. This result suggests that the substitution of Co into site B enhances the catalytic activity in methane combustion.

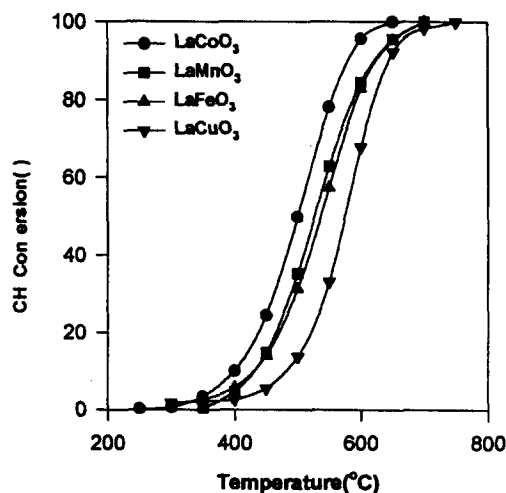


Fig. 5. Catalytic activity in methane combustion with various perovskite catalysts: $\text{CH}_4=1$ vol%, $\text{O}_2=4$ vol%, $\text{GHSV}=30000$ hr^{-1} .

Fig. 6 shows the effect of the substitution of Sr into site A and Co into site B of LaFeO_3 . The substitution of Sr into site A enhanced the catalytic activity and that of Fe into site B also enhanced the activity at a substitution ratio of 0.2, however, the catalytic activity decreased at a substitution ratio of 0.4.

It is well known that an oxygen ion can move through a lattice vacancy in a perovskite-type oxide, plus the mobility of the ion increases and the activation energy of the anion mobility decreases as the lattice vacancy increases²⁴. Consequently, the oxygen vacancies will increase following the removal of oxygen by a reducing agent on the surface as the mobility of the oxygen ion increases in the lattice. In the TPD results on the oxygen in the $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ oxide, the amount of oxygen desorbed at a low temperature increased as the amount of Fe increased²⁶. It would appear that the oxygen species (α -oxygen) desorbed at

a low temperature are reversible oxygen species which are involved in the complete oxidation reaction through being able to freely move in the lattice of metal oxides. Moon et al.²⁷⁾ reported that the expansion of a lattice by the addition of Co facilitates the reduction of oxygen by lowering the bond energy between the α -oxygen species and the metal.

With an increase in the Co content, it is difficult to reduce the oxygen owing to other factors in addition to lattice expansion. It has been previously reported that the amount of irreversible oxygen increases with an increase in the Co content followed by the holding of the peripheral oxygen in the lattice, thereafter, the α -oxygen species decreases relatively²⁷⁾. As shown in Fig. 6, the catalytic activity decreased relative to a decrease in the α -oxygen species in the Co content ≥ 0.4 .

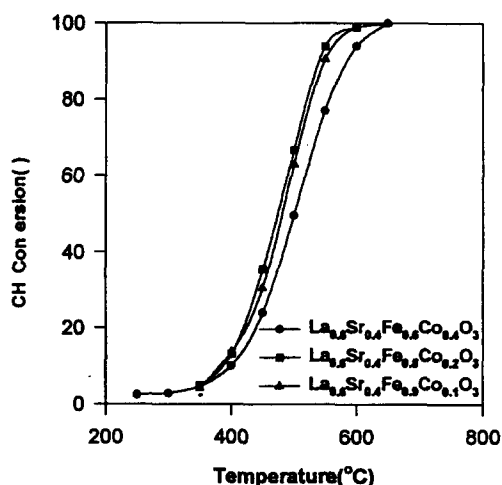


Fig. 6. Catalytic activity in methane combustion with various perovskite catalysts: $\text{CH}_4=1$ vol%, $\text{O}_2=4$ vol%, $\text{GHSV}=30000$ hr^{-1} .

Fig. 7 shows the TPR results of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ -type catalysts. These catalysts showed a large reduction peak, originating from the α -oxygen species, at 450°C . In addition, the peak sizes were exhibited in the order of $x=0.2 > 0.1 > 0.4$ in the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ -type catalysts. These results show the same tendency as the catalytic activity in methane combustion, and suggest that the partial substitution of Co into site B facilitates an increase in reversible lattice

oxygen, thereby increasing the catalytic activity in methane combustion, however, the catalytic activity decreased relative to a decrease in the α -oxygen species in the Co content ≥ 0.4 .

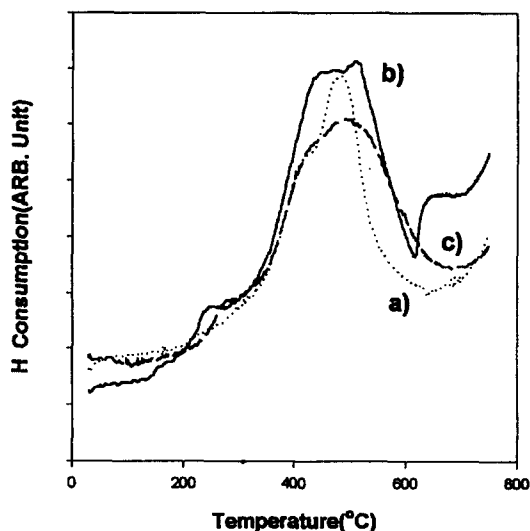


Fig. 7. TPR profiles measured for various perovskite-type oxides calcined at 600°C for 12 hs (heating rate = 10 K/min, gas mixture = 7.5% H_2/N_2):

- a) $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_3$,
- b) $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$,
- c) $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_3$.

3.4. Effect of Preparation Method of Catalysts

It is well known that the catalytic activity will differ according to the preparation method. In this study, two types of perovskite oxide were prepared in order to compare the properties of the catalysts relative to their preparation method. The results are shown in Fig. 8.

The catalysts prepared using the malic acid method exhibited a much lower T_{50} than those prepared using the solid state reaction method. The methane was completely exhausted at about 600°C on the catalyst prepared by the malic acid method, while the temperature increased to 800°C on the catalyst prepared by the solid state reaction method. It would appear that the active site of the former increases owing to its high surface area. Therefore, this result suggests that the catalyst prepared using the malic acid method can be used effectively in methane combustion.

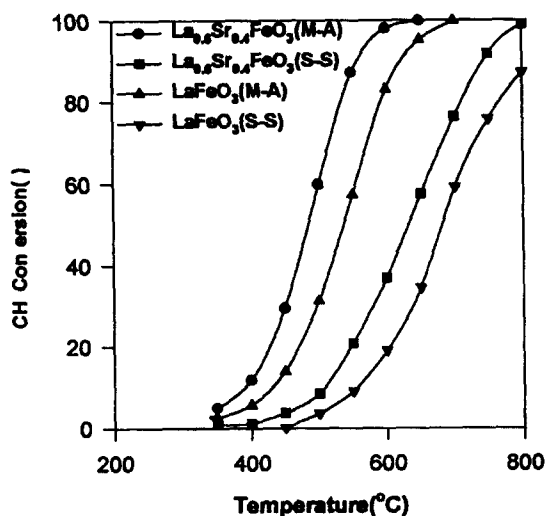


Fig. 8. Catalytic activity in methane combustion with various perovskite catalysts prepared by different methods: $\text{CH}_4=1$ vol%, $\text{O}_2=4$ vol%, $\text{GHSV}=30000$ hr^{-1} , M-A=malic acid method, S-S=solid state reaction method.

3.5. Effect of Reaction Conditions

It is well established that catalytic combustion can burn cleaner?? methane-air mixtures compared to gas-phase combustion. This study examined the effect of methane concentration on the methane combustion reaction. The results are shown in Fig. 9. In this case, a different partial pressure of methane was obtained by changing the volumetric flow rate of the carrier gas while maintaining a constant methane-oxygen ratio(1/4).

The catalytic activity was enhanced with a decreasing partial pressure of methane. It would seem that the ease with which the methane molecules made contact with the active site of the catalyst was relative to a decreasing methane concentration. In addition, it is well known that this reaction is exothermic and the combustion heat is difficult to control with an increasing methane concentration. Therefore, this result suggests that it is profitable to reduce the methane concentration.

The effect of space velocity on the methane combustion over $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ was examined and the results are shown in Fig. 10. In this case, a different space velocity was obtained by changing the mass of the catalyst while maintaining a constant volumetric flow rate.

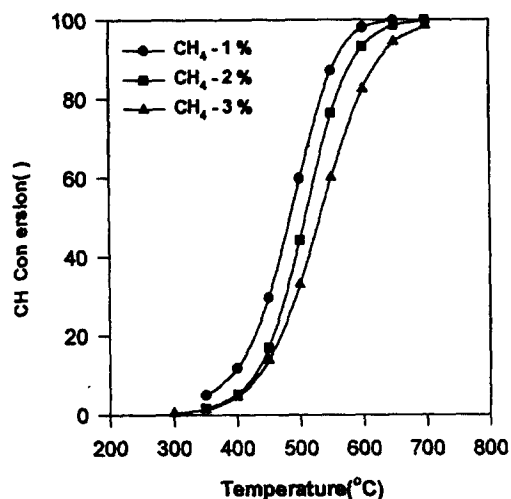


Fig. 9. Catalytic activity in methane combustion with various perovskite catalysts as a function of methane concentration: $\text{GHSV}=30000$ hr^{-1} .

The T_{50} decreased with a decreasing space-velocity, that is, an increased contact time between the catalyst and reactants. Similar results have been found with almost all other catalysts^{28,29}. Therefore, in the design of a catalytic converter and the scale-up of a reactor, the space velocity in the catalytic activity should be considered as very important.

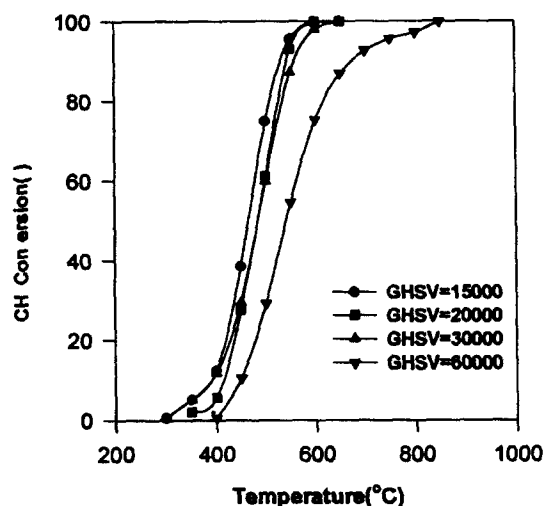


Fig. 10. Catalytic activity in methane combustion with various perovskite catalysts as a function of space velocity: $\text{CH}_4=1$ vol%, $\text{O}_2=4$ vol%.

4. Conclusions

The following conclusions were made based on the current study of methane combustion in the presence of oxygen over perovskite-type oxides.

1. With the LaFeO_3 -type catalyst, the partial substitution of Ba or Sr into site A enhanced the catalytic activity in the methane combustion. With the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -type catalyst, the catalytic activity showed a maximum value at $x=0.4$ plus the light-off temperature decreased above $x=0.4$.

2. With the LaBO_3 (B=Co, Fe, Mn, Cu)-type catalyst, the catalytic activity was exhibited in the following order $\text{Co} > \text{Fe} \approx \text{Mn} > \text{Cu}$. In addition, the partial substitution of Co into site B enhanced the catalytic activity, however, an excess amount of Co decreased the activity.

3. The surface area and catalytic activity of the perovskite catalysts prepared using the malic acid method showed higher values than those prepared using the solid reaction method.

4. The catalytic activity enhanced with a decreasing methane concentration and with a decrease in the space velocity

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