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# Catalytic combustion of $CH_4$ and CO on $La_{1-x}M_xMnO_3$ perovskites

Kwang-Sup Song[a,*], Hao Xing Cui[b], Sang Don Kim[c], Sung-Kyu Kang[a]

[a]*Korea Institute of Energy Research, PO Box 103, Yusong, Taejon, 305-343, South Korea*
[b]*Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, China*
[c]*Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon, South Korea*

## Abstract

The activities of perovskites depend on compositions and preparation methods. Various perovskites, $La_{1-x}M_xMnO_3$ (M=Ag, Sr, Ce, La), have been prepared by two different methods (co-precipitation and spray decomposition). The new preparation method, spray decomposition, produced perovskites of a high surface area of over 10 $m^2/g$. The catalytic activities for $CH_4$ and CO oxidation have been studied on a series of catalysts, $La_{1-x}M_xMnO_3$. The perovskite-type oxide, $La_{0.7}Ag_{0.3}MnO_3$, shows the highest catalytic activity: the complete conversion of CO and $CH_4$ at 370 and 825 K, respectively.

*Keywords:* Catalytic combustion; Perovskite; $CH_4$ oxidation; CO oxidation; Ag

## 1. Introduction

Oxidation catalysts for application in exhaust gas clean up were mainly noble metals. However, they are susceptible to sintering and too expensive. In 1972, Voorhoeve et al. [1] reported that perovskite-type oxides ($ABO_3$) showed a high catalytic activity comparable to that of a platinum catalyst for automotive exhaust. In perovskite-type oxides, substitution of A- and/or B-site cations by foreign metal cations brings about modification of catalytic properties. The effects of A-site substitution on the catalytic properties have been extensively studied by many researchers [1–7]. So far, substitution of rare-earth cations by K, Ca, Sr, Ba, Pb, Ce or Hf cations (A-site substitution) was reported in the literature for oxidation reactions [5–7]. Nevertheless substitution of rare-earth cations by Ag cation in perovskite-type oxides has not been reported as yet.

The perovskite-type oxides dealt with in the literature were synthesized most often by ceramic [8], co-precipitation [9], spray drying [10], freeze-drying methods [11] and amorphous citrate methods [12,13]. A high surface area and good chemical homogeneity of perovskites can be obtained by the freeze-drying and amorphous citrate method among various preparatory methods.

In the present work, we have tested a new and simple method, spray decomposition, for perovskite-type oxides synthesis. This method combines the spray drying and the amorphous citrate method. We have investigated the effects of Ag, Sr or Ce cation substitution for La in $LaMnO_3$, since $LaMnO_3$ shows a relatively high catalytic activity. We have also studied

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*Corresponding author. Tel.: +82-42-860-3611; fax: +82-860-3134; e-mail: kssong@sun330.kier.re.kr

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the catalytic activity of $La_{1-x}Ag_xMnO_3$ with a variation of $x$.

## 2. Experimental

### 2.1. Catalysts

Perovskite-type oxides were prepared by the conventional co-precipitation and the new spray decomposition. In case of the co-precipitation method, appropriate amounts of metal nitrates were dissolved in distilled water. Precipitation from the solution was performed with oxalic acid and ammonium carbonate. The resulting precipitate was filtered, washed with distilled water, dried at 393 K for 5 h and finally decomposed at 723 K in air for 2 h. After a thorough grinding in a mortar, the powdered solids were pelletized under a pressure of 400 kg/cm$^2$. Pelletized oxides were calcined at 1073 K for 4 h and then crushed to obtain 20–40 mesh particles.

In the spray decomposition method, which combines the spray drying and amorphous citrate method, excess citric acid was added to the metal nitrate solution to replace all the nitrate groups. Mixtures were then sprayed into a quartz tubular reactor (850 mm ID × 1200 mm length) maintained at a temperature of 823 K. Spraying of the solution of the metal ions into the furnace led to small droplets, which dried instantly followed by decomposition of the complexed metal ions. The spray decomposition method thus prevents the mixed oxide from segregating to different components. The homogeneous mixing of oxides is aimed at so as to increase the specific surface area and the catalytic activity. Oxides thus formed were ground, pelletized and calcined at 973 K for 4 h.

### 2.2. Apparatus and measurement

The activities of the catalysts were measured in a continuous flow reactor at atmospheric pressure. A 15 mm ID quartz tube served as reactor. Six K-type thermocouples were used to measure the temperature. One thermocouple was placed in front of catalyst bed to control the temperature of the furnace, and others were inserted into the catalyst bed 2.8 mm apart from each other to monitor the temperature of the catalyst bed. The amount of catalyst used was 3 ml (about 2.5 g). The feed gas was a mixture of 1% CO/air for CO oxidation and a mixture of 1% $CH_4$/air for methane oxidation. The feed gas passed downward through catalyst pellets (200–40 mesh). The gas flow rate was adjusted to obtain 10 000 h$^{-1}$ of gas hourly space velocity (GHSV). The effluent gases ($CO_2$, CO and $CH_4$) were analyzed by gas chromatography with TCD (column: Carboxen 1000, 60/80 mesh, $1/8'' \times 15'$).

X-ray powder diffraction (XRD) data were obtained with a diffraction spectrometer (Rigaku RTP 300RC), using Cu $K_\alpha$ radiation. The presence of the perovskite-type structure was confirmed from ASTM data. Surface areas of the samples were measured by the BET method ($N_2$ adsorption).

## 3. Results and discussion

### 3.1. Comparison of preparation methods

Because of the importance of surface area for the catalytic activity, various preparation methods were investigated to maximize the surface area of perovskite-type oxides. The conventional methods such as the freeze-drying methods and the amorphous citrate method have some disadvantages in that the procedure is complex and expensive. As mentioned earlier, the spray decomposition procedure combining the spray drying and amorphous citrate method is simple to apply and cheap in cost.

Fig. 1 shows the $CH_4$ oxidation rates of $LaMnO_3$ and $La_{0.7}Ag_{0.3}MnO_3$ catalysts prepared by spray decomposition and co-precipitation methods. It is seen that the $CH_4$ oxidation rates of both catalysts prepared by spray decomposition are higher than those prepared by co-precipitation. Fig. 2 shows the XRD patterns of $LaMnO_3$ catalysts prepared by spray decomposition and co-precipitation. The catalysts prepared by spray decomposition give a well crystallized single phase of $LaMnO_3$ after calcination at 873 K. Within the catalyst prepared by co-precipitation, crystalline perovskite-type oxide was, however, not detected unless the mixed oxides were calcined at temperatures above 1073 K. Some crystalline $La_xO_3$ was present even after calcination at 1173 K. Specific surface areas of perovskite-type oxides are listed in Table 1. The surface areas of perovskite-type oxides prepared by spray decomposition are higher than those prepared by co-precipitation. Perovskite-type oxides having the highest surface area (44 $m^2/g$) were prepared by the amorphous citrate method [13,14]. The freeze-drying method also can yield high surface area perovskite-type oxides (about 20 $m^2/g$) [11]. The samples studied here have surface area between 12 and 18 $m^2/g$. From our experimental results, it is noteworthy that the perovskite-type oxides prepared by spray decomposition exhibit even a better catalytic activity and that the spray decomposition method is comparable to the amorphous citrate and/or freeze-drying method.

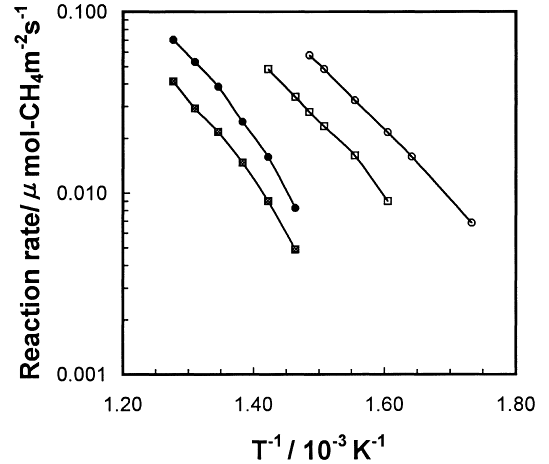

Fig. 1. $CH_4$ oxidation rates on the perovskite-type oxides prepared by spray decomposition and co-precipitation: (○) $La_{0.7}Ag_{0.3}MnO_3$ prepared by spray decomposition; (●) $La_{0.7}Ag_{0.3}MnO_3$ prepared by co-precipitation; (□) $LaMnO_3$ prepared by spray decomposition; and (■) $LaMnO_3$ prepared by co-precipitation.

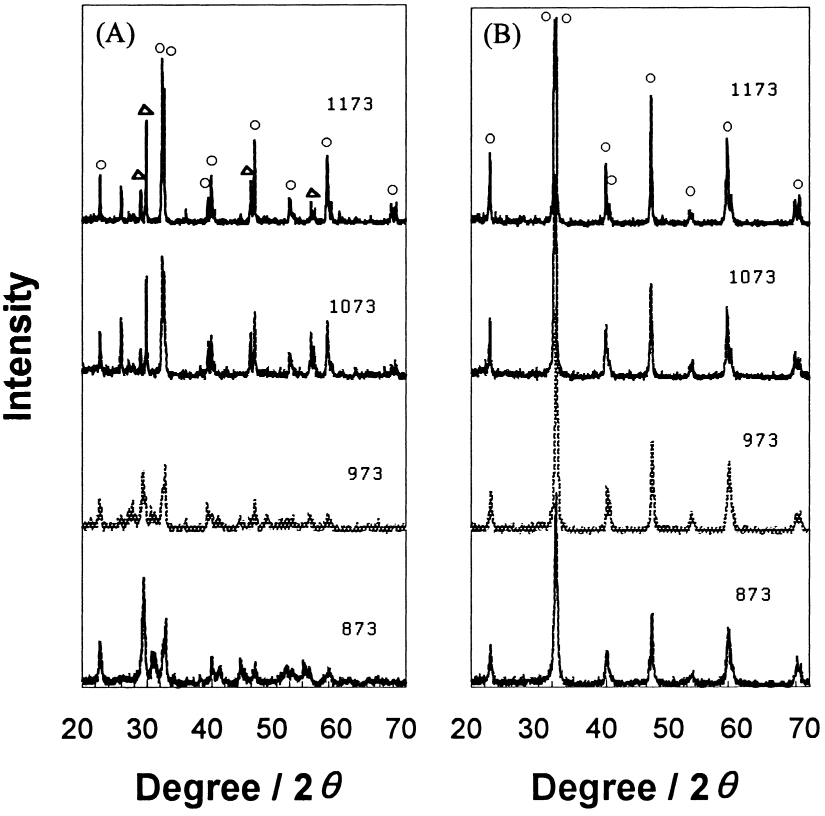

Fig. 2. XRD patterns of $LaMnO_3$ perovskites calcined at different temperatures: (A) $LaMnO_3$ prepared by co-precipitation; (B) $LaMnO_3$ prepared by spray decomposition. (○) perovskite, and (△) $La_2O_3$.

### 3.2. *Effects of the calcination temperature*

The perovskite structure is not established uniformly at very low calcination temperature. High-temperature calcination yields perovskite of a low

Table 1
Specific surface area of perovskite-type oxides

| Sample | Spray decomposition | | Co-precipitation | |
|---|---|---|---|---|
| | $T^a$ (K) | BET[b] ($m^2 g^{-1}$) | $T^a$ (K) | BET[b] ($m^2 g^{-1}$) |
| $LaMnO_3$ | 873 | 14.62 | 873 | 7.84 |
| $LaMnO_3$ | 973 | 12.20 | 973 | 8.83 |
| $LaMnO_3$ | 1073 | 8.79 | 1073 | 9.41 |
| $LaMnO_3$ | 1173 | 4.21 | 1173 | 5.11 |
| $LaMnO_3$ | 1273 | 2.11 | 1273 | 2.61 |
| $La_{0.9}Ag_{0.1}MnO_3$ | 973 | 16.34 | | |
| $La_{0.8}Ag_{0.2}MnO_3$ | 973 | 16.50 | | |
| $La_{0.7}Ag_{0.3}MnO_3$ | 973 | 18.60 | 1073 | 6.54 |
| $La_{0.6}Ag_{0.4}MnO_3$ | 973 | 17.40 | | |
| $La_{0.7}Sr_{0.3}MnO_3$ | 973 | 18.34 | | |
| $La_{0.7}Ce_{0.3}MnO_3$ | 973 | 18.69 | | |

[a] Calcination temperature.
[b] Specific surface area.

surface area of perovskite leading to a low catalytic activity. In general there is an optimal calcination temperature to achieve a high catalytic activity.

Fig. 3 shows the catalytic activities of $LaMnO_3$ produced by spray decomposition and co-precipitation for $CH_4$ oxidation. The reaction rate per unit surface area of oxides prepared by spray decomposition increased with an increase of calcination temperature as far as a single-phase perovskite-type oxide was formed. It is also seen that the maximum conversion of $CH_4$ on the catalysts prepared by the two different methods was obtained at a calcination temperature of 973 K. Zhang et al. [14] reported a trend similar to our results with the amorphous citrate method . A maximum catalytic activity was observed when the oxides were calcined at 873 K.

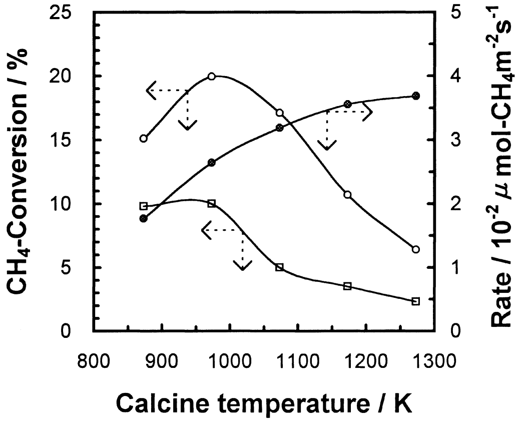

Fig. 3. Effects of calcination temperature on $CH_4$ oxidation activity of $LaMnO_3$ (reaction temperature: 673 K). (○, ●) $LaMnO_3$ prepared by spray decomposition, and (□) $LaMnO_3$ prepared by co-precipitation.

The surface area of $LaMnO_3$ calcined at different temperatures is also listed in Table 1. It is seen that the surface area of the $LaMnO_3$ catalyst from spray decomposition was higher than that from co-precipitation at low calcination temperatures. It has been reported that the specific surface area of oxides prepared by the amorphous citrate method passes through a maximum at a calcination temperature of 923 K [14]. The specific surface area of oxides prepared by co-precipitation showed a maximum at a calcination temperature of 1073 K. The specific surface area of perovskite-type oxides from spray decomposition, however, decreased monotonously with rising calcination temperatures and became almost equal to that of the oxides from co-precipitation calcined at 1173 K. Investigation of the various effects of the operational parameters in the spray decomposition method has permitted us to achieve that perovskite-type oxides have good catalytic activities at a calcination temperature of 973 K (4 h).

### 3.3. Effects of A-site substitution on the catalytic activity

The catalytic activities for oxidation and the related properties were generally changed by substitution of La in $LaMnO_3$. In this study, substituted perovskites have been prepared by partial substitution of $La^{3+}$ with $Ag^{+}$, $Sr^{2+}$ and $Ce^{4+}$. Substitution of Sr and Ce has been reported in the literature, but substitution of Ag has been rare as mentioned in Section 1. The activities of these catalysts for $CH_4$ oxidation are shown in Fig. 4, in which the highest temperature inside the catalytic bed is considered as the reaction temperature. The maximum temperature in the catalytic bed shifted from down-stream to up-stream as the reaction temperature increased. It can be noticed that the catalytic activity increased remarkably by the substitution of Ag. The effect of Sr substitution was not profound as compared to that of Ag substitution.

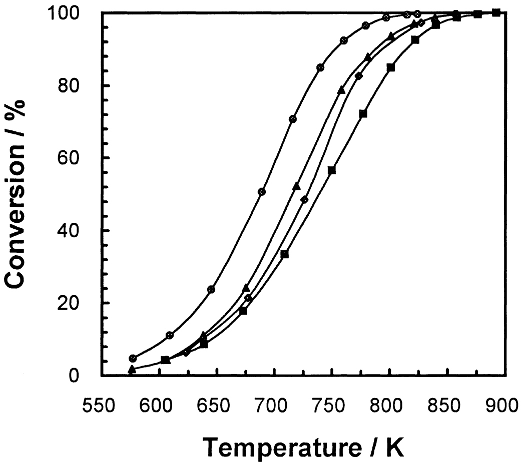

Fig. 4. Catalytic activities of $CH_4$ oxidation over $La_{0.7}M_{0.3}MnO_3$ prepared by spray decomposition: (◆) $LaMnO_3$; (●) $La_{0.7}Ag_{0.3}MnO_3$; (■) $La_{0.7}Ce_{0.3}MnO_3$; and (▲) $La_{0.7}Sr_{0.3}MnO_3$.

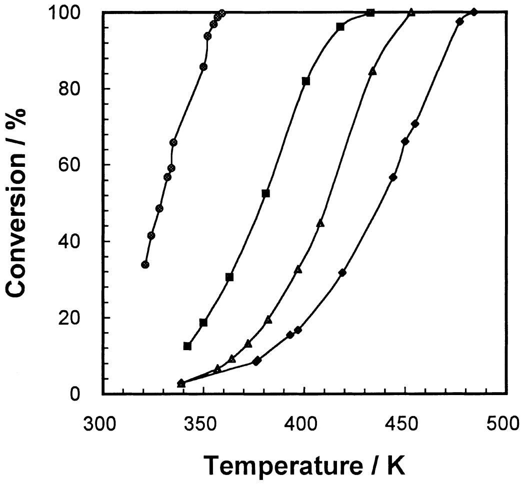

Fig. 5. Catalytic activities of CO oxidation over $La_{0.7}M_{0.3}MnO_3$ prepared by spray decomposition: (◆) $LaMnO_3$; (●) $La_{0.7}Ag_{0.3}MnO_3$; (■) $La_{0.7}Ce_{0.3}MnO_3$; and (▲) $La_{0.7}Sr_{0.3}MnO_3$.

Nitadori et al. [7] reported that Sr, Ce and Hf substitution for La in $LaMnO_3$ improved the catalytic activity for propane oxidation. They argued that the catalytic activity of perovskite-type oxides varied with the nonstoichiometry and the surface properties according to substitution of A-site in $ABO_3$. Although our experimental results with $CH_4$ oxidation were similar, the catalytic activity of $La_{0.7}Ce_{0.3}MnO_3$ is lower than that of $LaMnO_3$. The catalytic activities of $La_{0.7}M_{0.3}MnO_3$ increased in the order of Ag>Sr>La>Ce. With $La_{0.7}Ag_{0.3}MnO_3$, complete oxidation was observed at 825 K under reaction conditions.

Fig. 5 shows the catalytic activities for CO oxidation over $La_{0.7}M_{0.3}MnO_3$ catalysts. Similar to the $CH_4$ oxidation the highest activity of CO oxidation was obtained with the $La_{0.7}Ag_{0.3}MnO_3$ catalyst. The increasing order of activity for the $La_{0.7}M_{0.3}MnO_3$ catalysts in the catalytic CO oxidation, however, is Ag>Ce>Sr>La. With $La_{0.7}Ag_{0.3}MnO_3$, it was seen that the onset of oxidation occurred even at ambient temperature and complete combustion at 370 K. Imamura et al. [15] reported on the oxidation of CO on Mn/Ag composite oxides. A Mn/Ag composite catalyst showed the highest catalytic activity in CO oxidation below 673 K. The catalytic activity of this catalyst, however, decreased remarkably at higher reaction temperatures, since Ag in this catalyst is aggregated in metallic state. It should be noted that the catalytic activity and morphology of our $La_{0.7}Ag_{0.3}MnO_3$ catalyst did not change much at temperatures up to 1073 K.

### 3.4. *Effects of Ag content on the catalytic activity of $La_{1-x}Ag_xMnO_3$*

Substitution of La in $LaMnO_3$ by Ag causes an increase of oxidation activity as shown in Figs. 4 and 5. Catalytic activities of $La_{1-x}Ag_xMnO_3$ ($x$=0.1, 0.2, 0.3 and 0.4) catalysts were measured to assess the effect of the Ag content on the activity in the $CH_4$ oxidation. These catalysts were prepared by spray decomposition followed by calcination at 973 K. Fig. 6 shows the temperatures at which the $CH_4$ conversion reached 10% or 90% as a function of Ag content. It was of note that the highest activity of $La_{1-x}Ag_xMnO_3$ is exhibited at $x$=0.3. The change of activities of $La_{1-x}Ag_xMnO_3$ perovskites when $x$ is greater than 0.2 was moderate.

Activities of these catalysts for CO oxidation have also been measured. In Fig. 7, the temperatures at which the conversion of CO becomes 50% are shown as a function of Ag content. The effect of Ag substitution in $LaMnO_3$ on the CO oxidation was more profound as compared to that on $CH_4$ oxidation. The highest activity of $La_{1-x}Ag_xMnO_3$ is observed at $x$=0.3 similar to $CH_4$ oxidation. In addition, the high-

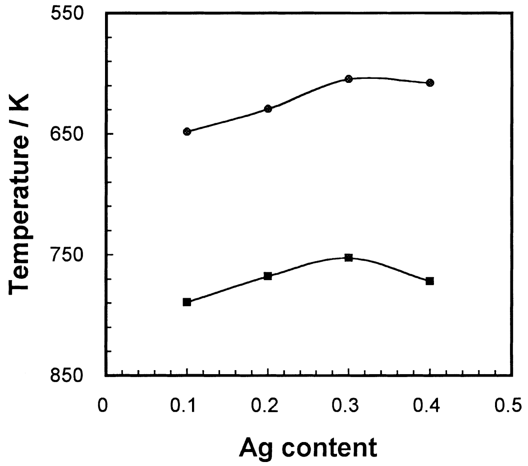

Fig. 6. The temperature of 10% or 90% $CH_4$ conversion as a function of Ag content in $La_{1-x}Ag_xMnO_3$: (■) 90% conversion; and (●) 10% conversion.

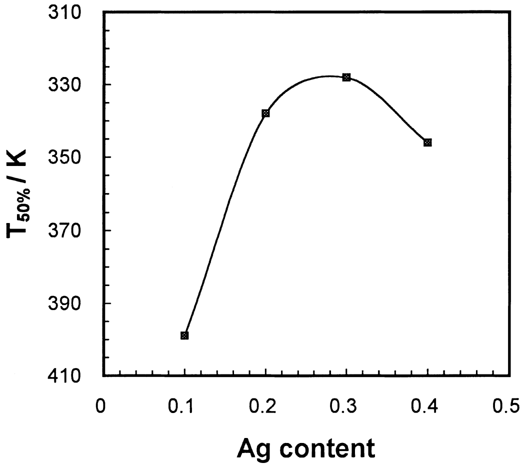

Fig. 7. The temperature of 50% CO conversion as a function of Ag content in $La_{1-x}Ag_xMnO_3$.

est surface area of perovskite, $La_{0.7}Ag_{0.3}MnO_3$, was displayed at $x$=0.3.

## 4. Conclusions

The spray decomposition method results in a uniform perovskite structure even at low calcination temperatures. The catalytic activities for the oxidation of CO and $CH_4$ are high with oxides prepared according to this method. With the spray decomposition procedure a calcination temperature of 973 K (4 h) was optimal to provide good catalytic activities. The catalytic activity of CO and $CH_4$ oxidation on the $La_{0.7}Ag_{0.3}MnO_3$ catalyst from spray decomposition was superior to that on the $La_{0.7}Sr_{0.3}MnO_3$ catalyst, which has been known to have a high catalytic activity of hydrocarbon oxidation. It is expected that $La_{0.7}Ag_{0.3}MnO_3$ would be a good candidate for application of perovskite-type oxides in industrial catalytic processes, such as exhaust gases clean up and catalytic combustion at low temperature.

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