Catalysis Letters 49 (1997) 65–68

Preparation and characterization of Ag / MnO_x / perovskite catalysts for CO oxidation

Kwang-Sup Song*, Sung-Kyu Kang and Sang Done Kim [a]

Catalytic Combustion Research Team, Korea Institute of Energy Research, Taeduk Science Town, Taejon 305-343, Korea
[a] *Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Taeduk Science Town, Taejon 305-701, Korea*

Received 16 July 1997; accepted 11 September 1997

The spray decomposition method with lanthanum nitrate, manganese nitrate, silver nitrate and citric acid was used to synthesize Ag- and Mn-incorporated perovskites. The resulting samples were characterized by X-ray diffraction, BET adsorption measurement, X-ray photoelectron spectroscopy, and temperature-programmed oxygen desorption (O_2-TPD) measurement. The obtained composite Ag / MnO_x / perovskites catalysts exhibit higher activity by a few orders of magnitude at 338 K than that of $LaMnO_3$. From the O_2-TPD measurement, the high activity of the Ag / MnO_x / perovskites may result from the increase of weak oxygen adsorption below 373 K.

Keywords: Ag, perovskite, CO oxidation, spray decomposition, Ag / MnO_x / $LaMnO_3$

1. Introduction

The catalytic oxidation of CO is an important reaction for the treatment of factory effluent gas and automobile exhaust. Most of the catalysts for oxidation of CO are expensive noble metals. Therefore, relatively cheap transition metals compounds such as metal oxides, spinels, perovskites and alloys have been developed as the potential catalysts for catalytic combustion.

Novel synthesis of perovskites has been an ongoing research interest since Meadowcroft [1] reported the use of strontium doped $LaCoO_3$ as a low cost oxygen electrode material comparable to Pt [2–8]. Oxidation of CO over perovskites has been widely studied as a probe reaction for surface characterization. It has been reported that CO oxidation over perovskites occurs mainly in the temperature range of 373–523 K [9–11]. Substitution of A- and / or B-site cation with foreign metal in ABO_3 perovskites can modify catalytic properties significantly [12–14].

The mixed metal oxide composite consisting of Ag and Mn has also been known to have a high activity for oxidation of CO [15]. The spill-over of the atomically adsorbed oxygen from Mn to Ag was suggested to increase the oxidation activity. However, the rate of CO oxidation decreased with increasing temperature above 673 K due to the agglomeration of Ag.

In this study, the composite catalysts compromising of perovskites, Ag and Mn have been prepared by using the spray decomposition method to increase the thermal stability with higher catalytic oxidation activity of CO at lower temperatures.

2. Experimental

2.1. *Catalysts preparation*

Ag / MnO_x / perovskites were synthesized by using the spray decomposition method. The metal nitrate salts ($AgNO_3$, $La(NO_3)_3$, $Mn(NO_3)_2$) and an equivalent amount of citric acid were dissolved in doubly distilled water. The obtained solution was sprayed into the quartz tubular reactor (850 mm i.d. × 1200 mm length) at 823 K. The concentration and flow rate of the solution were 0.1 M and 5 ml / min, respectively. Drying and decomposition occurred simultaneously in the reactor. The obtained powder was pelletized and calcined subsequently in a furnace at 973 K for 4 h.

2.2. *Catalyst characterization*

X-ray powder diffraction (XRD) data were obtained with a Rigaku RTP 300RC instrument using Cu $K\alpha$ radiation. The surface area of powders was measured by the nitrogen adsorption at 77 K in the BET method (Micromeritics ASAP2000). The oxygen desorption in the samples was determined by the temperature-programmed desorption method by using an on-line quadrupole mass spectrometer (Vacuum Generator, model 560). The sample was heated up to 773 K under vacuum and cooled down to room temperature. The sample was exposed to oxygen at 1.0 atm and 273 K for 30 min in a sampling bottle. The reversibly adsorbed oxygen on perovskite was evacuated by vacuum at 273 K. In the O_2-TPD experiment, the ramping rate was 10 K min^{-1}. The binding energy of Mn $2p_{3/2}$ was estimated by using the XPS (Leybold LHS-10) with respect to the binding energy of C 1s, 284.5 eV as a standard.

---

* To whom correspondence should be addressed.

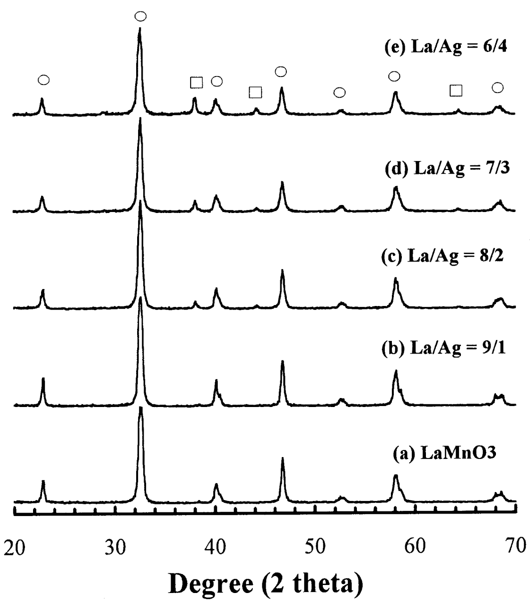

Figure 1. X-ray diffraction pattern of Ag/MnO$_x$/perovskites; (○) $LaMnO_3$ perovskite and (□) Ag metal.

2.3. Catalytic activity measurement

The known amount of catalyst, 1 cm^3 (about 0.8 g), was charged in a quartz tubular reactor (15 mm i.d.). The feed gas (mixture of 1% CO/air) was introduced from the top of the reactor through a packed bed of catalyst pellets (20–40 mesh) at a gas hourly space velocity (GHSV) of 30,000 h^{-1}. The effluent gas was analyzed by gas chromatography (HP5890, Hewlett Packard) equipped with TCD using Carboxen 1000 column (60/80 mesh, 1/8″ × 15″).

3. Results and discussion

The XRD patterns of Ag/MnO$_x$/perovskites prepared by the spray decomposition method are shown in figure 1. The X-ray diffraction pattern of $LaMnO_3$ exhibits the perovskite structure without other separate metal oxides according to the ASTM cards, as found previously [16]. With the increase of Ag loading in the sprayed solution, the peaks of X-ray diffraction corresponding to Ag-metal appear that may suggest the partial Ag-substitution into the perovskite structure.

The perovskites synthesized from the spray decomposition method have higher surface areas compared to those obtained from the coprecipitation method as shown in table 1. Also, the change of surface area as a function of calcination temperature is shown in figure 2. As can be seen, the perovskites from the spray decomposition method attain high surface area up to 1073 K. The surface area of perovskites synthesized from spray decomposition decreases with increasing calcination temperature above 1173 K as the perovskites synthesized from the coprecipitation method.

The catalytic activity of Ag/MnO$_x$/perovskites for CO oxidation is much higher than that of $LaMnO_3$ perovskite without a variation of the apparent activation energy, as can be seen in figure 3. Also, the reaction rate over Ag/MnO$_x$/perovskites for CO oxidation at 338 K is given in table 1. As can be seen, the reaction rate over the Ag/MnO$_x$/perovskite (Ag/La = 3/7) is much higher than that of the $LaMnO_3$ perovskite.

The catalytic activities of the Ag/MnO$_x$/perovskite (Ag/La = 3/7) and $LaMnO_3$ are shown in figure 4. Complete CO oxidation over the Ag/MnO$_x$/perovskite (Ag/La = 3/7) can be attained below 373 K, whereas the same level of conversion on $LaMnO_3$ can be attained at 523 K. The maximum reaction rate of CO oxidation over Ag/MnO$_x$/perovskites is obtained with the Ag/La ratio of 3/7. The reaction rate decreases with a further increase of Ag substitution for La in $LaMnO_3$, as can be seen in table 1.

From the XPS measurements of the oxidation state of Mn perovskites, no significant variation of the binding energy of the Mn $2p_{3/2}$ level before and after the incorporation of Ag is observed (table 1). This may reflect there is no practical electronic interaction between Ag and Mn in perovskites.

The temperature-programmed oxygen desorption (O_2-TPD) spectra of Ag/MnO$_x$/perovskites (Ag/La = 0 and 3/7) are shown in figure 5. No evolution of lattice oxygen from $LaMnO_3$ perovskite can be found in the present study. Contrary to $LaMnO_3$, the atomically

Table 1
The BET surface area, the reaction rate at 338 K and the binding energy of Mn $2p_{3/2}$ of Ag/MnO$_x$/perovskites

Sample	S_{BET} ($m^2 g^{-1}$)	r_{CO} (μmol CO $m^{-2} s^{-1}$)	Mn $2p_{3/2}$ (eV)
$LaMnO_3$	12.2 (8.8)[a]	0.2	641.5
Ag/MnO$_x$/perovskite (Ag/La = 1/9)	16.3	0.9	–
Ag/MnO$_x$/perovskite (Ag/La = 2/8)	16.5	9.5[b]	641.4
Ag/MnO$_x$/perovskite (Ag/La = 3/7)	18.3 (6.4)	19.1[b] (19.4[c])	641.4
Ag/MnO$_x$/perovskite (Ag/La = 4/6)	17.4	17.1[b]	–

[a] The value in parentheses indicates the surface area of the sample obtained from the coprecipitation method.
[b] Estimated by extrapolating the reaction rate to 338 K in Arrhenius plots in figure 3.
[c] After thermal treatment in air for 50 h.

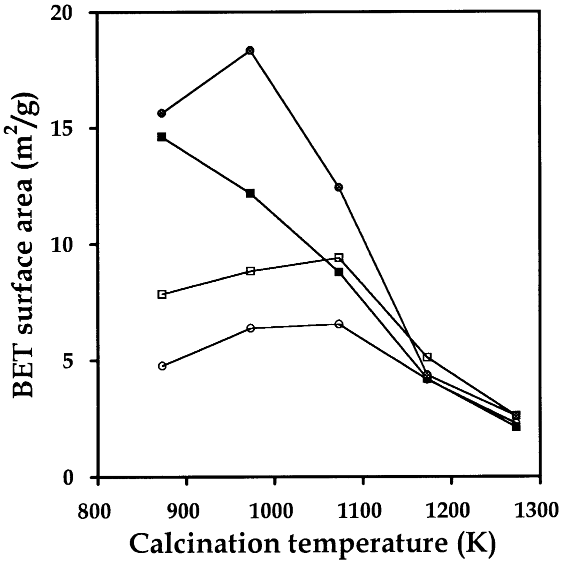

Figure 2. Change of BET surface area of Ag/MnO$_x$/perovskites as a function of calcination temperature; (○) Ag/MnO$_x$/perovskites from the coprecipitation method, (□) LaMnO$_3$ from the coprecipitation method, (●) Ag/MnO$_x$/perovskites from the spray decomposition method and (■) LaMnO$_3$ from the spray decomposition method.

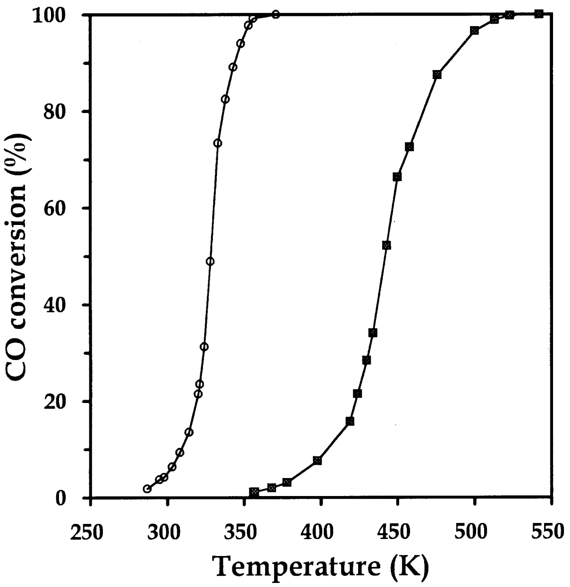

Figure 4. The conversion of CO oxidation over perovskites as a function of reaction temperature; (○) LaMnO$_3$ and (■) Ag/MnO$_x$/perovskite (Ag/La = 3/7) under the reaction conditions; S_V = 30,000 h^{-1} and 1% CO in air.

adsorbed β-oxygen desorbs significantly from Ag/MnO$_x$/perovskite (Ag/La = 3/7) at the temperature range of 400–653 K. Especially, the oxygen desorption from Ag/MnO$_x$/perovskite (Ag/La = 3/7) is unique since the amount of weakly adsorbed oxygen below 400 K is much larger than that of β-oxygen. It has been known that the rate of CO oxidation over perovskites depends much on surface reaction between the chemisorbed CO and O$_2$ at the lower CO concentration ranges [17]. Under the present experimental conditions, the rate of adsorbed oxygen ([O$*$] or [O$*$O], $*$ = adsorption site) formation may affect the overall reaction rate. It may claim that the presence of the weakly adsorbed oxygen contributes remarkably to increase the CO oxidation rate over the Ag/MnO$_x$/perovskite (Ag/La = 3/7). Therefore, Ag/MnO$_x$/perovskite (Ag/La = 3/7) seems

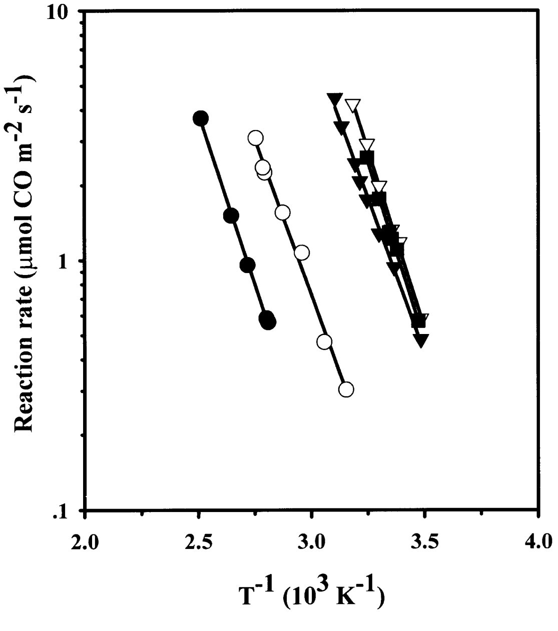

Figure 3. Arrhenius plot for the CO oxidation over Ag/MnO$_x$/perovskites; (●) Ag/La = 0/10, (○) Ag/La = 1/9, (▼) Ag/La = 2/8, (▽) Ag/La = 3/7 and (■) Ag/La = 4/6.

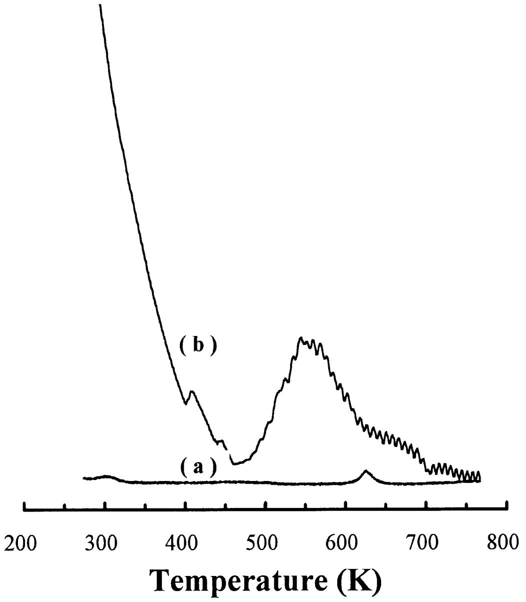

Figure 5. Temperature-programmed desorption spectrum of oxygen (m/e = 32) from (a) LaMnO$_3$ and (b) Ag/MnO$_x$/perovskite (Ag/La = 3/7). The ramping rate was 10 K min^{-1}.

to have the suitable ensemble for oxygen adsorption at lower temperatures.

After thermal treatment in air at 973 K for 50 h (table 1), there is no resultant decrease of catalytic activity for Ag/ MnO_x /perovskite (Ag/La = 3/7), in agreement with a previous report that the catalytic activity of perovskite for CO oxidation did not change after thermal treatment in air [18]. It may reflect that the rare earth metals in perovskites provide thermal stability of transition metal oxides for the high temperature application. The resulting Ag/ MnO_x /perovskite from the high temperature calcination (973 K) produces much higher thermal stability than the simple binary metal oxide composites [15]. This high thermal stability and the comparable reaction rate of CO oxidation at lower temperatures can be great benefits for the effluent gas treatment.

4. Conclusion

The Ag/ MnO_x /perovskites (Ag/La = 3/7) were synthesized by using the spray decomposition method with metal nitrates and citric acid. The obtained composite Ag/ MnO_x /perovskites catalysts exhibit higher activity by a few orders of magnitude at 338 K than that of $LaMnO_3$. This composite catalyst based on perovskite appears to enhance lower temperature adsorption of oxygen, thereby improving the catalytic activity of CO oxidation.

Acknowledgement

The authors acknowledge a grant-in-aid for research from the R&D Management Center for Energy and Resources, Korea.

References

[1] D.B. Meadowcroft, Nature 226 (1970) 847.
[2] W.F. Libby, Science 171 (1971) 499.
[3] J.L.G. Fierro, J.M.D. Tascon and L.G. Tejuca, J. Catal. 93 (1985) 83.
[4] N. Mizuno, H. Fujii, H. Igarashi and M. Misono J. Am. Chem. Soc. 114 (1992) 7151.
[5] H.M. Zhang, Y. Shimizu, Y. Teraoka, N. Miura and N. Yamazoe, J. Catal. 121 (1990) 432.
[6] J. Kirchnerova, D. Klvana, J. Vaillancourt and J. Chaouki, Catal. Lett. 21 (1993) 77.
[7] L.G. Tejuca, J.L.G. Fierro and J.M.D. Tascon, in: *Advances in Catalysis*, Vol. 36, eds. D.D. Eley, H. Pines and P.B. Weisz (Academic Press, San Diego, 1989) p. 237.
[8] B. Viswanathan, in: *Properties and Applications of Perovskite-type Oxides*, eds. L.G. Tejuca and J.L.G. Fierro (Dekker, New York, 1993) ch. 13.
[9] J.M.D. Tascon, S. Mendioroz and L.G. Tejuca, Z. Phys. Chem. NF 124 (1981) 109.
[10] N.J.H. Voorhoeve, J.P. Remeika and L.E. Trimble, Ann. NY Acad. Sci. 272 (1976) 3.
[11] T. Simizu, Nippon Kagaku Kaishi (1981) 1525.
[12] T. Nitadori, S. Kurihara and M. Misono, J. Catal. 98 (1986) 221.
[13] N. Yamazoe and Y. Teraoka, Catal. Today 8 (1990) 175.
[14] H. Arai, T. Yamada, K. Eguchi and T. Seiyma, Appl. Catal. 26 (1986) 265.
[15] S. Imamura, H. Sawada, K. Uemura and S. Ishida, J. Catal. 109 (1988) 198.
[16] K.S. Song, H.X. Cui, S.D. Kim and S.K. Kang, *Proc. 3rd Int. Workshop on Catalytic Combustion*, Amsterdam 1996.
[17] S. Rajadurai and J.J. Carberry, J. Catal. 147 (1994) 594.
[18] K. Tabata and M. Misono, Catal. Today 8 (1990) 249.