

Effect of Samarium on the Thermal Stability and Activity of the Mn/Ag Catalyst in the Oxidation of CO

There have been many reports on catalytic oxidation of carbon monoxide with respect to prevention of air pollution. Various kinds of catalysts are involved such as precious metals (1, 2), base metal catalysts (3, 4), and composite base metal catalysts (5, 6). Some catalysts containing silver such as Mn/Cu/Co/Ag and Mn/Co/Ag composite oxides are also active (7, 8). However, details of the action of silver or other constituents are not known. We clarified that the high activity of manganese–silver composite oxide catalysts was due to the cooperative action of Mn and Ag (9). When active oxygen on Ag was consumed in the oxidation of CO, lattice oxygen of Mn was immediately transferred to the reduced Ag, thus maintaining the active oxidized state of Ag. The Mn acted as an oxygen reservoir. Therefore, silver in the composite catalysts was protected from deactivation due to metallization and aggregation at temperatures about 400°C at which single component silver oxides readily aggregate to metallic state.

Although the manganese–silver composite catalysts have considerable thermal stability as described above, they must endure more severe operating conditions in order to be used as practical combustion catalysts. Previously, we found that an addition of a small amount of samarium improved the thermal stability and activity of transition metal oxides of the first series in the periodic table (10, 11). In this work the manganese–silver composite catalyst was treated at high temperatures under a reducing atmosphere, and the effect of samarium on the stability of this catalyst was investigated.

The manganese–silver composite oxide

(molar ratio: 80/20) and the manganese–silver–samarium composite oxide (molar ratio: 80/20/5) were prepared as follows. The former was designated as Mn/Ag (80/20) and the latter as Mn/Ag/Sm (80/20/5), respectively. A known amount of manganese(II) nitrate and silver(I) nitrate [and samarium(III) nitrate] were dissolved in deionized water. Sodium hydroxide (3 *N*) was added to the solution with stirring until its pH was about 12. The resultant precipitate was washed several times until its pH was below 9. The precipitate was dried at 100°C overnight. The dry precipitate was molded into a disk and was calcined in air at 450°C for 3 h. The catalysts were cut into about 15 mesh size before use. The manganese oxide catalyst (designated as the Mn catalyst) was prepared from manganese(II) nitrate by the same procedure described above. It was identified as Mn₂O₃ by X-ray diffraction analysis.

Reaction was carried out using an ordinary flow reactor under atmospheric pressure. Heat treatment of the catalysts under reducing atmosphere was carried out as follows. One milliliter of the catalysts was placed in the reactor under a flow of 98% N₂ plus 2% CO (SV: 10000 h⁻¹) and the temperature of the catalyst bed was increased from room temperature to prescribed values (400, 600, 750, 850, and 950°C) at a rate of 3.75°C/min. Heat treatment at those temperatures was carried out for 3 h. The catalysts thus treated were provided for CO oxidation using the same reactor. The composition of the reaction gas was CO: 1%, O₂: 18%, and N₂: 81% (SV: 10,000 h⁻¹). The temperature of the catalyst bed was increased from room temperature at a rate of 3.75°C/min. The concentration of

CO at the exit of the reactor was monitored, and the activity of the catalysts was evaluated by the temperatures at which the conversion of CO reached 10% (T_{10}), 50% (T_{50}), and 95% (T_{95}). The reaction was not affected by any mass transfer limitation in the CO conversion range less than 50% because the rate of the reaction was independent of the particle size of the catalyst used.

The temperature-programmed desorption (TPD) of oxygen from the catalysts was carried out using a quartz reactor connected to an ordinary vacuum line. The Mn catalyst, Mn/Ag (80/20), and Mn/Ag/Sm (80/20/5) were heated in oxygen at 400°C for 2 h. After cooling to room temperature in oxygen, the gas phase was evacuated for 1 h. Helium was introduced into the reactor (35 ml/min) and the catalyst bed was increased to 950°C at a rate of 5°C/min. The amount of desorbed oxygen was monitored by a thermal conductivity detector. Calibration was made on the basis of the amount of desorbed oxygen from pure Ag₂O in the temperature range from 200 to 500°C. After the first cycle of the TPD procedure described above, the catalysts were again heated in oxygen at 400°C for 2 h. The catalysts thus treated were again tested for the second TPD of oxygen in order to determine their ability to recover the lattice oxygen.

Carbon monoxide was determined using a Shimadzu GC-3BT gas chromatograph equipped with a thermal conductivity detector. The column packing consisted of Celite 545 (1.7 m) plus molecular sieve of 5 Å (1.3 m), and the column temperature was 90°C. The X-ray, SEM, and EDX analyses were carried out using a Rigaku Denki Geigerflex 2012 X-ray analyzer, a Hitachi S-2100 scanning electron microscope, and a Philips EDAX 9100 equipped with a Shimadzu EMX-SM electron probe microanalyzer, respectively.

Figure 1 shows the effect of heat treatment under reducing atmosphere (CO 2% plus N₂ 98%) on the catalytic activity of the Mn catalyst, Mn/Ag (80/20), and Mn/Ag/

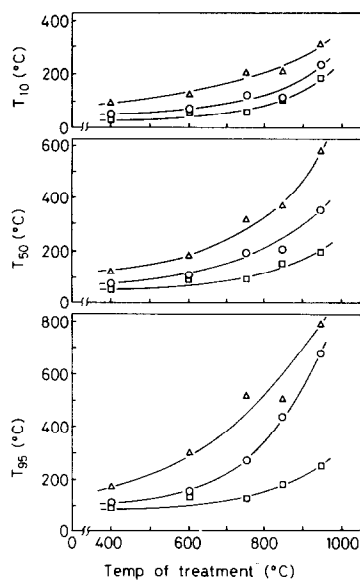


Fig. 1. Oxidation of CO over the Mn catalyst, Mn/Ag (80/20), and Mn/Ag/Sm (80/20/5) treated in a reducing atmosphere at various temperatures. [CO] = 1%; [O₂] = 18%; [N₂] = 81%; SV = 10,000 h⁻¹; (Δ) Mn catalyst; (○) Mn/Ag (80/20); (□) Mn/Ag/Sm (80/20/5); Temperatures of heat treatment in 2% CO plus 98% N₂ for 3 h.; T_{10} , T_{50} , and T_{95} are the temperatures at which CO conversions reached 10, 50, and 95%, respectively.

Sm (80/20/5) in the oxidation of CO. Activity of the catalysts was compared on the basis of T_{10} , T_{50} , and T_{95} , respectively. As the temperature of heat treatment increased, the activity of all catalysts decreased. Irrespective of the temperature of heat treatment, the activity was always in the order, Mn catalyst < Mn/Ag (80/20) < Mn/Ag/Sm (80/20/5). Comparison of the Mn catalyst and Mn/Ag (80/20) shows that a combination of Ag with Mn is still effective even under the severe reaction conditions. The effect of Sm was clearly seen for the catalysts treated above 700°C. A 95% conversion of CO was observed at 240°C for Mn/Ag/Sm (80/20/5) after heat treatment at 950°C, while reaction temperature above 680°C was necessary for Mn/Ag (80/20) to attain the same conversion.

Figure 2 shows the change of BET surface areas of the catalysts on heat treat-

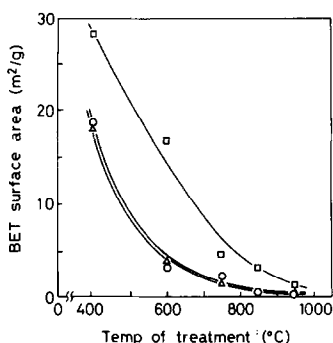


FIG. 2. BET surface area of the catalysts. (Δ) Mn catalyst; (\circ) Mn/Ag (80/20); (\square) Mn/Ag/Sm (80/20/5); Temperatures of heat treatment in 2% CO plus 98% N_2 for 3 h.

ment. The surface area of Mn/Ag/Sm (80/20/5) was always larger than those of the Mn catalyst and Mn/Ag (80/20). Figure 3 exhibits the temperature profiles of the reactions catalyzed by the three catalysts treated at 950°C. Specific rates (rates per unit surface area of the catalysts) are also plotted in a low CO conversion range (less than 15%) to satisfy the condition of the differential reactor. A remarkable difference in the activity can be seen among the three catalysts as judged from the CO conversion curves. However, specific rates did not differ so much between Mn/Ag (80/20) and Mn/Ag/Sm (80/20/5), being a little larger for the latter, although the comparison was limited in a narrow CO conversion range. This shows that the large surface area of Mn/Ag/Sm (80/20/5) as shown in Fig. 2 was one of the causes of the high activity of this catalyst.

Previously we reported that Sm inhibited the grain growth of 3d transition metal oxides at high temperatures and maintained their large surface areas (10, 11). The SEM analysis indicated that the bulk state of Mn/Ag/Sm (80/20/5) treated at 950°C as observed by its sectional view was rougher than that of Mn/Ag (80/20) although the photographs are not shown here. This fact and the result shown in Fig. 2 were in accordance with the previous conclusion.

That is, an addition of Sm maintained the large surface area of Mn/Ag (80/20) by retarding its grain growth.

Figure 4 exhibits the SEM photographs of the surface of the catalysts. A number of large silver crystals were observed on the surface of Mn/Ag (80/20), while aggregation of silver metal for Mn/Ag/Sm (80/20/5) was not remarkable. An optical microscopic photograph indicated that the interior of the particle of Mn/Ag (80/20) was divided into three layers, showing the inhomogeneous nature of the bulk (Fig. 5). This was supported by the result of the EDX analysis that the concentration of silver at points A, B and C were found to be 21, 16, and 19 mol%, respectively. No such heterogeneous distribution of silver was observed throughout the bulk of Mn/Ag/Sm (80/20/5).

The X-ray diffraction analysis of Mn/Ag/Sm (80/20/5) treated at 950°C indicated the presence of MnO, metallic Ag, and Sm_2O_3 . However, no other diffraction peak suggesting the existence of the interaction among Mn, Ag, and Sm was obtained. This was also in accordance with the previous

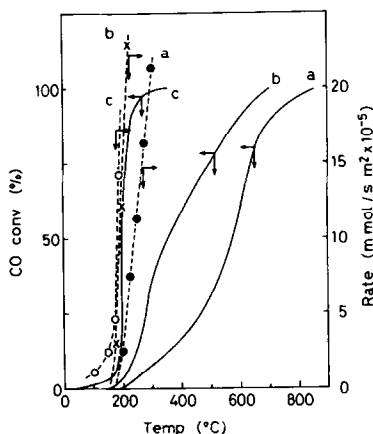
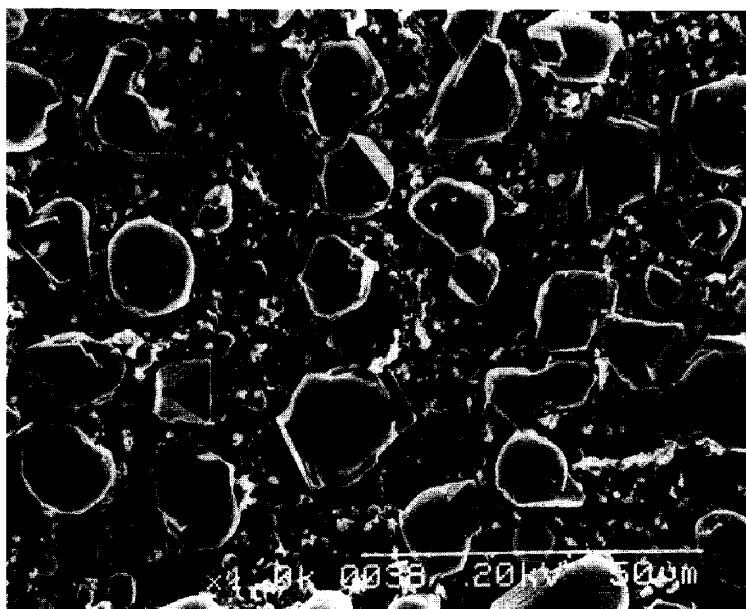
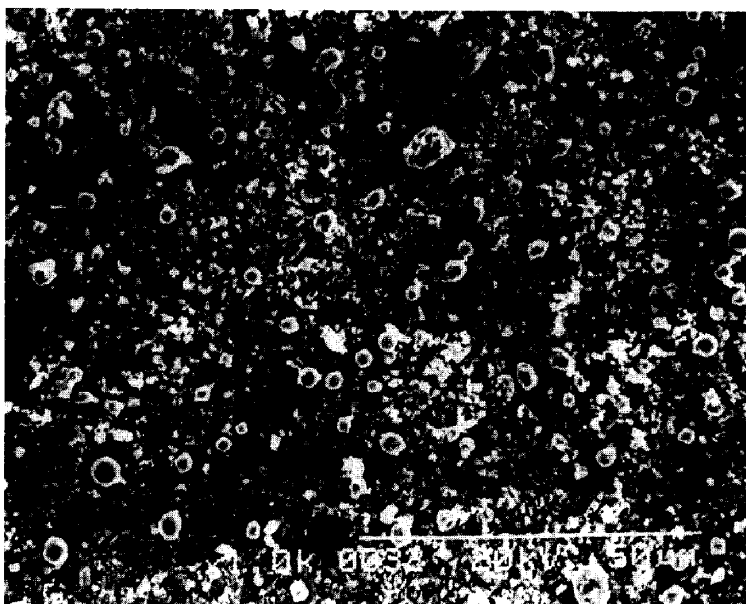


FIG. 3. Oxidation of CO over the Mn catalyst, Mn/Ag (80/20), and Mn/Ag/Sm (80/20/5) treated at 950°C in 2% CO plus 98% N_2 for 3 h. The reaction condition is the same as described in Fig. 1. (a) Mn catalyst; (b) Mn/Ag (80/20); (c) Mn/Ag/Sm (80/20/5); (—) CO conversion; (---) Specific rate (rate per unit surface area of the catalysts).



50 μ m

Mn / Ag (80 / 20)



50 μ m

Mn / Ag / Sm (80 / 20 / 5)

FIG. 4. SEM photographs of the surface of the catalysts treated at 950°C in 2% CO plus 98% N₂ for 3 h.

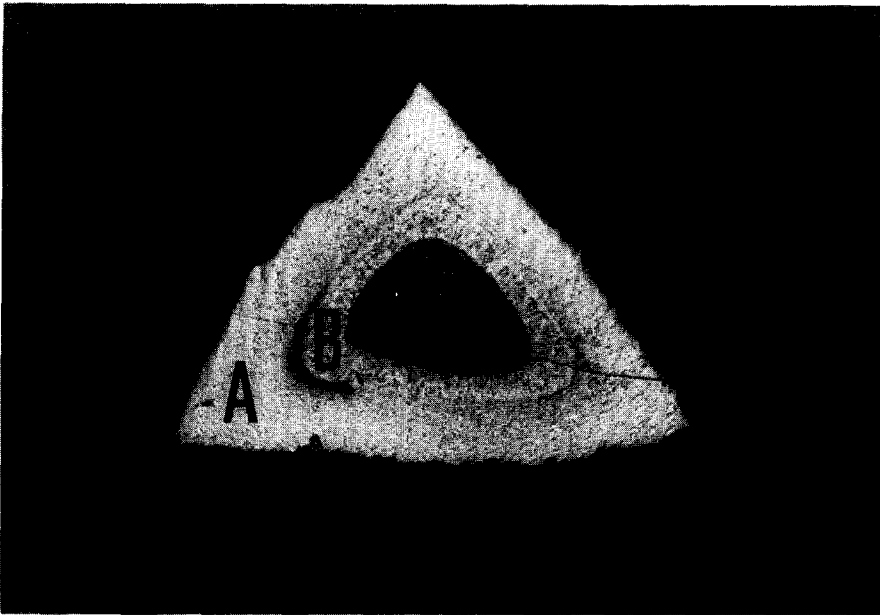


FIG. 5. Optical microscopic photograph and EDX analysis of Mn/Ag (80/20) treated at 950°C in 2% CO and 98% N₂ for 3 h. Ag = 21 mol% (A), 16 mol% (B), 19 mol% (C).

result that Sm inhibited grain growth of transition metal oxides by producing heterophases (mainly Sm₂O₃) in the bulk of the oxides (11).

Generally, heat treatment of oxide catalysts under reducing atmosphere results in the reduction of the oxides and, at the same time, in the grain growth of the oxide crystals. In the absence of Sm, grain growth of manganese oxides proceeds extensively and the oxides become dense. Therefore, reduced Ag will be expelled from the bulk and aggregated as large crystals on the surface or it may migrate toward the center of the catalyst particle (Figs. 4 and 5). Reduction of silver oxides to the metallic state also occurs in the presence of Sm. However, as grain growth of the bulk manganese oxides is not remarkable, metallized Ag can still be homogeneously dispersed throughout the manganese oxide matrix. Retention of dispersed state of Ag in the Mn matrix will be favorable for the Mn/Ag catalyst to exhibit high performance in the oxidation of CO.

Figure 6 shows the TPD curves and Table 1 shows the amount of desorbed oxygen from the catalysts heated from room temperature to 950°C. The form of the starting Mn catalyst and that of Sm in Mn/Ag/Sm (80/20/5) calcined at 450°C were Mn₂O₃ and Sm₂O₃, respectively. As the valence state of Mn in the Mn/Ag catalyst calcined at

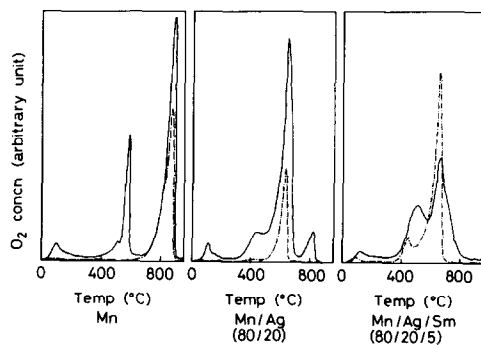


FIG. 6. TPD of oxygen. (—) First cycle: The catalysts prepared by calcination at 450°C for 3 h were further heated at 400°C in O₂ for 2 h. (---) Second cycle: After first cycle, the catalysts were heated at 400°C in O₂ for 2 h.

TABLE I
Amount of Oxygen Desorbed by Heating the Catalysts to 950°C in He^a

Cycle	Catalyst	Mn catalyst	Mn/Ag (80/20)	Mn/Ag/Sm (80/20/5)
1st ^b ($\times 10^{-3}$ g atom O)		6.37	6.53	5.87
2nd ^b ($\times 10^{-3}$ g atom O)		2.80	1.38	3.81
2nd/1st ^c (%)		44.0	21.1	64.9

^a One gram of the catalysts was used.

^b The procedure for the 1st and 2nd TPD cycles is described in Fig. 6.

^c Percentage of the amount of oxygen desorbed in the 2nd cycle relative to that in the 1st cycle.

450°C was 3.2 and Ag was in the form of Ag₂O (9), the starting Mn/Ag (80/20) and Mn/Ag/Sm (80/20/5) were assumed to be MnO_{1.6}(20/80)AgO_{0.5} and MnO_{1.6}(20/80)AgO_{0.5}(5/80)SmO_{1.5}, respectively. The final states of the catalysts after the first cycle of TPD were deduced as follows. As silver oxides lose their lattice oxygen easily (9), it was assumed that Ag in the composite catalysts was metallic after heating to 950°C. In a separate experiment using TG, it was found that Sm₂O₃ lost only 7% of its lattice oxygen by heating to 950°C in He. Therefore, from the amount of desorbed oxygen in the first cycle of TPD shown in Table I, the final states of the catalysts were determined as MnO_{0.99}, MnO_{1.01}(20/80)Ag, and MnO_{1.02}(20/80)Ag(5/80)SmO_{1.40}, respectively. Therefore, the final state of Mn was MnO in all cases. The Mn catalyst exhibited its main desorption peak at 870°C in addition to the small peak at 580°C. Therefore, Mn was converted to MnO completely at about 870°C. The Mn/Ag (80/20) and Mn/Ag/Sm (80/20/5) exhibited small peaks at about 460°C which were due to the lattice oxygen of Ag. In addition, a large peak was observed at about 650°C. As no other peak was observed above 800°C and Mn was converted completely to MnO, the peak at 650°C was due to the desorption of the lat-

tice oxygen of Mn forming MnO. The fact that lattice oxygen of Mn in Mn/Ag (80/20) and Mn/Ag/Sm (80/20/5) desorbed at a temperature more than 200°C lower than that at which Mn₂O₃ released its oxygen showed that the lattice oxygen of Mn became remarkably labile by the combination with Ag. This strongly supports the previous conclusion that lattice oxygen of Mn was easily transferred to Ag and was desorbed from Ag to oxidize CO (9).

Comparison of the behavior of Mn/Ag (80/20) and Mn/Ag/Sm (80/20/5) in the first cycle of TPD (Fig. 6) shows that the strength of the bond of the lattice oxygen of Mn/Ag/Sm (80/20/5) was more widely distributed than that of Mn/Ag (80/20). This may indicate the incomplete crystal growth of Mn/Ag/Sm (80/20/5) owing to the presence of Sm. In the second cycle of TPD, the amount of desorbed oxygen from Mn/Ag (80/20) corresponded to 21.1% of that in the first cycle, while 64.9% of oxygen based upon the first cycle desorbed in the case of Mn/Ag/Sm (80/20/5). Therefore, the recovery of lattice oxygen was much easier for the latter. An additional remarkable feature is that desorption of oxygen from Ag was observed for Mn/Ag/Sm (80/20/5) even in the second cycle, while scarce desorption occurred for Mn/Ag (80/20). As Ag was more finely dispersed in Mn/Ag/Sm, silver oxides could be recovered by heating at 400°C in oxygen. These results indicate that the lattice oxygen of Mn/Ag/Sm (80/20/5) was easily desorbed and recovered through finely dispersed Ag. Therefore, the lability of the lattice oxygen was assumed to be one of the causes for the higher activity of this catalyst compared to Mn/Ag (80/20) after heat treatment in a reducing atmosphere.

The results of the present work were summarized as follows:

(1) The lattice oxygen of manganese oxides in the Mn/Ag catalyst was easily transferred to and desorbed from Ag. This role of manganese oxides as the oxygen reservoir will help maintain the activity of the

catalyst when used in the highly oscillating condition between the oxidizing and reducing atmosphere as is the case for automobile exhaust gases (12).

(2) An addition of a small amount of Sm inhibited grain growth of manganese oxides treated at high temperatures in a reducing atmosphere, thus, leading to the retention of a large surface area.

(3) As the grain growth of the Mn/Ag/Sm catalyst was inhibited owing to the presence of Sm, Ag could be finely and homogeneously dispersed in the matrix of the catalyst. On the other hand, Ag aggregated on the surface as large crystals or migrated toward the center of the Mn/Ag catalyst particle.

(4) Therefore, the lattice oxygen of the Mn/Ag/Sm catalyst was more easily desorbed and recovered through dispersed Ag than that of the Mn/Ag catalyst, which resulted in the higher activity of the Mn/Ag/Sm catalyst.

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