

Oxidation of Carbon Monoxide Catalyzed by Manganese-Silver Composite Oxides

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The oxidation of carbon monoxide on Mn/Ag composite oxides was carried out and their catalytic action was investigated. The composite oxides had much higher activities than either the Mn or the Ag single oxide catalysts. The Ag in the composite catalyst remained in the oxidized state in air even at calcination temperatures as high as 400°C, as long as its content was less than 50 mol%, whereas it lost lattice oxygen in the absence of Mn at the same temperature. The TPD and TG analyses showed that the composite oxides had active lattice oxygen belonging to Ag which was easily liberated on heating in the absence of oxygen. It was found, however, that Ag still retained the oxidized states even after the desorption of its active lattice oxygen, but reduction of Mn occurred instead. These facts suggested that the active oxygen on Ag was mainly consumed in the oxidation of CO, and Mn served as an oxygen carrier; i.e., vapor phase oxygen was first incorporated into the composite catalyst through Mn and, then, was transferred to the reduced Ag. This concerted action of Mn and Ag in the composite catalyst provided high activity in the oxidation of CO. © 1988 Academic Press, Inc.

1. INTRODUCTION

The catalytic oxidation of carbon monoxide is an important object of research in an effort to reduce air pollution caused by exhaust gases such as those from automobile emission. The most efficient and commercially employed combustion catalysts are precious metals such as Pt, Pd, and Rh, and their catalytic behavior has been investigated extensively (1-3). Attempts have also been made to use base metal catalysts for the oxidation of CO because of the limited availability of precious metals (4, 5). As single component base metals cannot rival precious metals, improvement in their activity has been attempted by combining several elements. Such examples are perovskite-type catalysts (6-8), manganese-copper composite oxides (9, 10), or copper-chromium catalyst (11).

Silver, which is relatively abundant com-

pared to precious metals of the VIII group, is used as an oxidation catalyst in reactions of industrial importance such as epoxidation of ethylene and oxidation of methanol to formaldehyde (12, 13). It is not used as a combustion catalyst generally because of its thermal instability with respect to sintering during reactions at high temperatures. However, certain catalysts which are effective for the oxidation of CO contain silver as one of their components (14). Recently Haruta and Sano prepared Mn/Co/Ag composite catalysts which are highly active for the combustion of CO and hydrogen (15). As these catalysts contain manganese as well as silver, a combination of these two elements seems to be an important factor contributing to their activity, but details of the action of silver and manganese in these catalysts are not understood.

The present work deals with the oxidation of CO over Mn/Ag composite oxides, with attention being focused on the behavior of silver and manganese, and the interaction between them.

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2. EXPERIMENTAL

Catalyst Preparation

Manganese(II) nitrate and silver(I) nitrate at known molar ratios 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 with deionized water several times and was dried in air at 100°C overnight. The dry precipitate was molded into a disk and was calcined in air at prescribed temperatures for 3 h. The catalysts were crushed to about 15 mesh size before use.

Apparatus and Procedure

Reactions were carried out using an ordinary flow reactor under atmospheric pressure, and the amount of catalyst used was 1 ml. Unless otherwise stated, the composition of the reaction gas was CO: 1%, O₂: 18%, and N₂: 81%, and the gaseous hourly space velocity was 10000 h⁻¹. The temperature of the catalyst bed was increased from room temperature at a rate of 3.75°C/min using an electric furnace. The concentration of CO at the exit of the reactor was monitored by a gas chromatograph, and the catalytic activity was evaluated by the temperature at which the conversion of CO reached 98% (*T*₉₈). As the determination of *T*₉₈ during the course of the first cycle of temperature increase was inaccurate, *T*₉₈ was obtained as follows. After approximately 98% conversion of CO was attained, the temperature was decreased and, then, again increased. This procedure was repeated until an exact *T*₉₈ was assured. The accurate *T*₉₈ was determined in this manner within 30 min after the initial approximate 98% conversion of CO was attained.

The temperature programmed desorption (TPD) of oxygen from the catalysts was carried out using a glass reactor connected to an ordinary vacuum line. The Mn and Mn/Ag catalysts were heated in oxygen at 400°C (in the case of the Ag catalyst, 260°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 temperature of the catalysts was increased at a rate of 3.75°C/min. The amount of desorbed oxygen was monitored by a thermal conductivity detector.

Analysis

Carbon monoxide was determined using a Shimadzu GC-3BT gas chromatograph. The column packing consisted of Celite 545 (1.7 m) plus molecular sieve 5A (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, an Akashi MSM-9 scanning electron microscope, and a Shimadzu EMX-SM electron microprobe X-ray analyzer, respectively. Valence states of the elements were analyzed using a Shimadzu ESCA 750 spectrophotometer. The reductions of the catalysts with CO were carried out in a chamber of a Rigaku Denki TG thermobalance.

The average valence of Mn in the catalysts was determined as follows. A known amount of the catalyst was dissolved in a 3.6 N sulfuric acid solution of Mohr's salt (2.13 mg Fe²⁺/ml) which also contained Fe³⁺ to prevent reduction of Ag¹⁺ to Ag⁰. An aliquot of the solution was analyzed for the total concentration of Mn by complete oxidation of the Mn ions to Mn⁷⁺ with KIO₄, followed by colorimetric analysis at 527 nm. The residual solution was treated with hydrochloric acid to precipitate Ag as AgCl, which was removed by filtration. A known amount of 3.6 N aqueous sulfuric acid containing NH₄VO₃ (1.94 mg V⁵⁺/ml) was added to the solution, and the remaining V⁵⁺ was back-titrated with Mohr's salt using diphenylamine as an indicator. The average valence of Mn was calculated by

$$\text{Average valence} = 2 + b/a,$$

where *a* and *b* are the amounts of total Mn in the solution and Fe²⁺ consumed, both in moles, respectively.

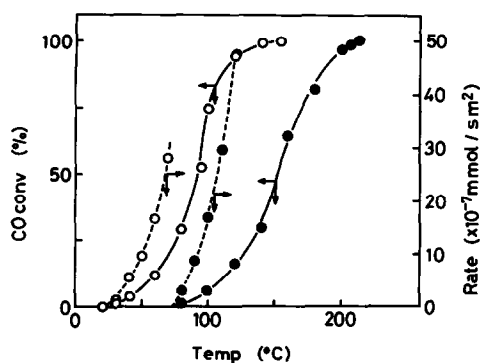


FIG. 1. Oxidation of CO over Mn and Mn/Ag (70/30) catalysts calcined at 400°C. [CO] = 1%; SV = 10,000 h⁻¹; (●) Mn catalyst; (○) Mn/Ag (70/30).

3. RESULTS AND DISCUSSION

Oxidation of CO by Mn, Ag, and Mn/Ag Catalysts

Figure 1 shows the typical temperature profiles of the reactions over manganese oxide (Mn catalyst) and Mn/Ag composite catalyst with 30 mol% Ag, both calcined at 400°C. The comparison of both CO conversion curves shows that the Mn/Ag catalyst had much superior performance than the Mn catalyst over the whole temperature range. Specific rates (rates per unit surface area of the catalysts) are also plotted in the figure. They were obtained only in a low CO conversion range (less than 20%) to satisfy the condition of differential reactor. The reactions were not affected by any mass transfer limitation at this low CO conversion range. It is clear that the inherent activity of the Mn/Ag catalyst was also much higher than that of the Mn catalyst.

The effect of the addition of Ag was further investigated for the catalysts calcined at 400 and 700°C, or dried at 100°C overnight (Fig. 2). In the case of the reactions over highly active catalysts dried at 100°C, the temperature of the catalyst bed often went up spontaneously at low CO conversion range due to the accumulation of the heat of reaction; thus it was very difficult to obtain specific rates at a given temperature. Therefore, the values of T_{98} were employed

in order to compare the activity of all catalysts although the comparison was rather qualitative.

The activity of the Mn catalyst calcined at 400°C increased remarkably by addition of Ag over a wide range of Ag content; T_{98} decreased from 200°C for the Mn catalyst to as low as 100°C for the composite catalyst containing 50 mol% of Ag. Addition of Ag increased the BET surface area of the catalysts, which was one of the promoting effects of Ag. However, it is not the main factor because, as shown in Fig. 1, the specific rate for the Mn/Ag catalyst was much larger than that of the Mn catalyst. Moreover, the mode of the change in the surface area on addition of Ag did not correspond to that of the change in the activity.

The promoting effect of Ag was observed only in the low concentration range for the catalysts calcined at 700°C. Silver aggregated probably in the metallic state at 700°C as deduced from the fact that white crystals of Ag were observed on the surface of the catalysts even with relatively low Ag loadings.

Catalysts dried at 100°C were remarkably active, especially in the higher Ag content

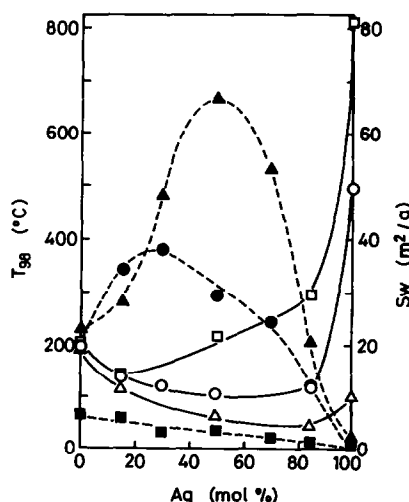


FIG. 2. Oxidation of CO by Mn/Ag catalysts. [CO] = 1%; SV = 10,000 h⁻¹; (—) T_{98} , (---) BET surface area (S_w). Calcination temperature: (△) 100°, (○) 400°C, (□) 700°C.

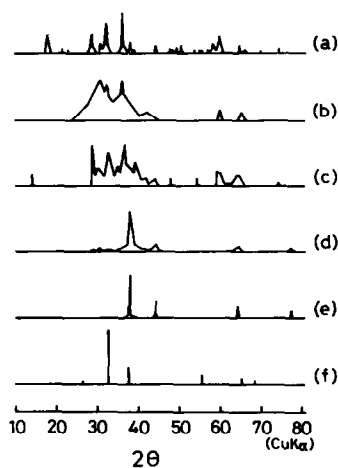


FIG. 3. X-ray diffraction patterns of the catalysts calcined at 400°C. (a) Mn catalyst, (b) Mn/Ag (70/30), (c) Mn/Ag (50/50), (d) Mn/Ag (30/70), (e) Ag catalyst, and (f) Ag₂O from literature values (18).

region. These catalysts, however, were unstable and deactivated during reaction as a result of aggregation of metallic Ag. Although CO was completely oxidized over the Ag catalyst at a temperature as low as 100°C, the activity decreased rapidly and T_{98} increased beyond 600°C after 40 min. Even though catalysts dried at 100°C had high initial activities, the following experiments were confined to those calcined at

400°C because of their stability during the oxidation reaction.

Characterization of the Catalysts Calcined at 400°C

Figure 3 shows the X-ray diffraction patterns of the catalysts calcined at 400°C. The Mn catalyst was identified as γ -Mn₂O₃. On addition of Ag the peaks become broad and unresolved, and the state of Ag could not be identified because of the lack of any clear peak due to Ag. On the other hand, the catalysts containing more than 50 mol% Ag only showed peaks due to metallic Ag.

The results of ESCA and chemical analyses of the catalysts are provided in Table 1. Although the average valence of Mn was 3 in the absence of Ag, it increased to 3.2 upon addition of less than 50 mol% of Ag. The catalyst with less than 50 mol% Ag showed an Ag MNN Auger peak at about 903.5 eV, and the position of the peak shifted to 902.8 eV at higher Ag contents. As Ag was metallic at more than 50 mol% Ag (X-ray analysis), the value of 902.8 eV was assigned to Ag metal. The Ag₂O exhibited an MNN Auger peak at 903.8 eV, which was near the range of values observed for the catalysts with less than 50 mol% (903.5–903.6 eV). Therefore, the Ag

TABLE I

ESCA and Chemical Analyses of the Catalysts Calcined at 400°C

Catalyst		Mn 2p _{3/2} (eV)	Ag MNN Auger peak ^a (eV)	Valence of Mn ^b	Surface Ag ^c (mol%)
Mn (mol%)	Ag (mol%)				
100	0	642.0	—	3.0	0
85	15	642.9	903.5	3.2	32.3
70	30	642.8	903.6	3.2	36.6
50	50	642.9	903.5	3.2	46.1
30	70	642.5	902.8	2.5	59.7
15	85	642.8	902.8	2.5	72.0
0	100	—	902.8	—	100

^a Ag MNN Auger peak for commercial Ag₂O was at 903.8 eV.

^b Chemical analyses.

^c ESCA analyses.

in the catalysts was in oxidation states corresponding nearly to Ag_2O . It has been reported that about 7% of the total lattice oxygen of Ag_2O is eliminated between 100 and 300°C, and metallic Ag crystallizes above 300°C (16). The present results show that oxidized states of silver are stabilized in the presence of Mn if its content is not large. The chemical analyses of the catalysts also provided the evidence that the catalysts with less than 50 mol% Ag contained only an oxidized form of Ag because no insoluble metallic Ag was observed during the analytical procedure using aqueous sulfuric acid. However, the ESCA analyses do not necessarily indicate the presence of a definite phase of Ag_2O , because the existence of Ag_2O could not be established by the X-ray diffraction data. Therefore, it should be emphasized that Ag was in the oxidized state which seemingly corresponded to Ag_2O .

When the Ag content was high and metallic Ag appeared, the average valence of Mn decreased from 3.2 to 2.5, but the change in the valence state of Mn was not reflected in the ESCA data. The decrease in Mn valence indicates that lattice oxygen of Mn was removed during the course of the reduction and aggregation of Ag, although Mn was stable as Mn_2O_3 in the absence of Ag. In the following experiments we used the catalyst containing 70 mol% Mn and 30 mol% Ag [Mn/Ag (70/30)] and investigated its catalytic behavior in detail. The surface Ag content in Mn/Ag (70/30) was 36.6% as determined by ESCA analysis. The EDX analysis also showed that the surface contained 33.4% Ag; thus the composition of the catalyst seemed almost uniform both in bulk and on the surface.

Oxidation of CO by Mn/Ag (70/30)

The dependence of the reaction rate on CO and O_2 concentrations was investigated both for Mn/Ag (70/30) and for the Mn catalyst (Mn_2O_3). The following results were obtained:

$$\begin{aligned} \text{Mn/Ag (70/30):} \quad \text{rate} &= kP_{\text{O}_2}^0 P_{\text{CO}}^{0.68} \\ E &= 12.0 \text{ kcal/mol} \end{aligned}$$

$$\begin{aligned} \text{Mn}_2\text{O}_3: \quad \text{rate} &= k'P_{\text{O}_2}^0 P_{\text{CO}}^{0.51} \\ E &= 11.2 \text{ kcal/mol.} \end{aligned}$$

The Mn/Ag (70/30) retained its activity after repeated uses at a reaction temperature of about 130°C, but the catalyst was deactivated under much more severe conditions. The value of T_{98} increased to 181°C after the reaction at 700°C for 2 h, and metallic Ag was clearly observed on the catalytic surface. The presence of 3 to 5% of carbon dioxide, which is usually contained in the exhaust gases, exhibited no effect on the activity of Mn/Ag (70/30). The CO_2 had a detrimental effect on the activity of Ag/ γ - Al_2O_3 which was obtained by mixing equal amounts of γ - Al_2O_3 and Ag which were dried at 100°C, followed by further calcination at 400°C. The conversion of CO at 142°C decreased from 98 to 81% in the presence of 5% carbon dioxide. This shows that Ag, when combined with Mn, was protected from poisoning by carbon dioxide. However, the comparison may not be valid because the former catalyst contained Ag in the oxide form and the latter catalyst contained metallic Ag. Water had a retarding effect on the Mn/Ag (70/30). The conversion of CO decreased from 98 to 82% in the presence of 11.6% H_2O at 130°C; however, the poisoning effect was not permanent, and the conversion recovered quickly after the injection of water ceased.

TPD of Oxygen Species on the Catalyst

Figure 4 shows TPD curves of oxygen from Mn/Ag (70/30), Mn, and Ag catalysts. The Mn catalysts exhibited a TPD peak from 60 to 210°C which corresponded to only 0.5% of the total lattice oxygen. This peak is attributed to an oxygen species adsorbed on the catalyst surface. In addition, a peak was observed at about 480°C which amounted to 7.8% of the total lattice oxygen. The Mn/Ag (70/30) catalyst had peaks at 50–200°C, at about 380°C, and above

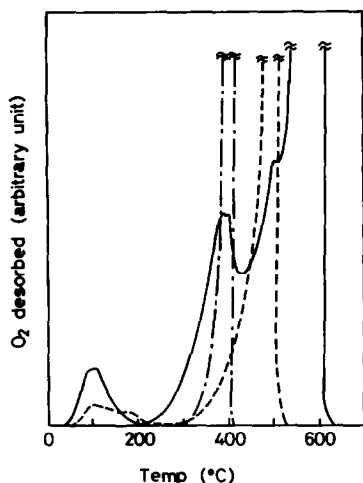


FIG. 4. TPD of oxygen from Mn catalyst (---), Mn/Ag (70/30) (—), and Ag catalyst (---). Mn catalyst and Mn/Ag (70/30) were heated in oxygen at 400°C, and Ag catalyst at 260°C before TPD procedure.

450°C. The first peak, attributed to surface oxygen species, corresponded to 1.0% of the total lattice oxygen. The second peak coincided with the desorption peak from the Ag catalyst. As the Ag catalyst was heated at 260°C in oxygen before the TPD procedure, its state was Ag_2O ; thus the peak at 380°C is due to desorption of its lattice oxygen to produce metallic Ag (16). Similarly, the peak at 380°C for Mn/Ag (70/30) is due to the oxygen belonging to Ag which is seemingly present at Ag_2O . The percentages of the amount of oxygen desorbed below 650°C with respect to the total lattice oxygen in the catalysts were 8.3 and 35.1% for the Mn and Mn/Ag (70/30) catalysts, respectively. Calculation of the amount of lattice oxygen in Mn/Ag (70/30) was based on the assumption that Ag was seemingly in the form of Ag_2O and Mn was in the form of $\text{Mn}_2\text{O}_{3.2}$, as determined by chemical analysis (Table 1). The results show that Mn/Ag (70/30) had more labile lattice oxygen than the Mn catalyst because of the presence of Ag.

TG Analyses on the Behavior of Lattice Oxygen

The behavior of the lattice oxygen was

further investigated in the chamber of a thermobalance by using CO as a reducing agent. The catalysts were first heated in oxygen at 400°C, and, then, the temperature was lowered to a prescribed temperature while introducing oxygen into the chamber. After oxygen was replaced by nitrogen, 10% CO in nitrogen was introduced and the reduction was started. The result of the reaction at 400°C is shown in Fig. 5. A decrease in the weight of the Mn catalyst began only after an introduction of CO. In the case of Mn/Ag (70/30), however, desorption of oxygen was observed just after the introduction of only nitrogen, and a further removal of oxygen was observed by introducing CO. The oxygen lost when nitrogen was introduced came from the lattice oxygen bonded to Ag in the composite oxide and seemed to correspond to that from Ag_2O shown by the TPD peak in Fig. 4. Although the desorption of lattice oxygen was an irreversible process to produce metallic Ag in the case of pure Ag_2O , adsorption and desorption of oxygen by Ag were observed repeatedly for Mn/Ag (70/30) by introducing oxygen and nitrogen alternatively at 400°C. This shows that Ag in the composite catalyst was prevented from an irreversible change to metallic Ag. The amount of oxygen lost corresponded to about 80% of the lattice oxygen of Ag,

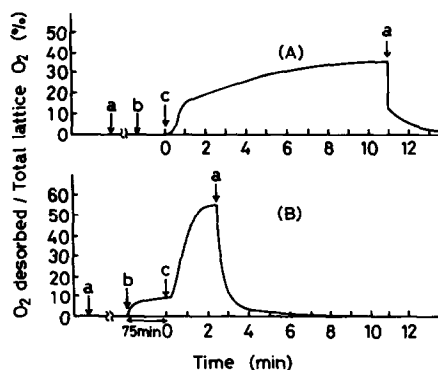


FIG. 5. Reduction of Mn catalyst (A) and Mn/Ag (70/30) (B) at 400°C. Introduction of (a) O_2 , (b) N_2 , and (c) CO 10% and N_2 90%.

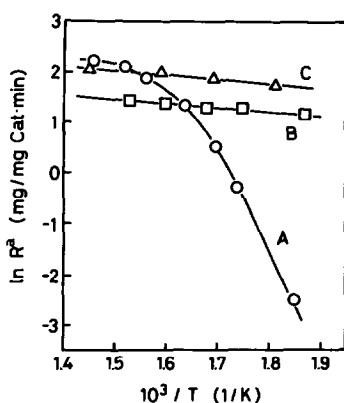


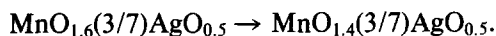
FIG. 6. Reduction of Mn catalyst (A), and Mn/Ag (70/30) (B and C) by 10% CO in nitrogen. R^a , rate of weight loss. Rates were measured at the points where 7.7% (curve A), 3.6% (curve B), and 22.0% (curve C) of the total lattice oxygen of the catalysts was removed.

present seemingly as Ag_2O in the composite catalyst.

Figure 6 shows the temperature dependence of the rate at which lattice oxygen was removed by CO. The rates for the Mn catalyst were measured at the point where 7.7% of its total oxygen was removed (curve A). The rates for Mn/Ag (70/30) were measured at two points, when 3.6% (curve B) and 22.0% (curve C) of total lattice oxygen was removed. The former corresponded to the point where 69.5% of the oxygen belonging to Ag, which was seemingly present as Ag_2O , still remained and the latter to the point where all oxygen in the Ag and 10.1% of the oxygen in the Mn were lost. The calculations were based on the assumption that all of the oxygen bonded to Ag was lost first. The rate of oxygen removal from the Mn catalyst was low in the lower temperature region, and the activation energy of the reaction was very large (41.0 kcal/mol). Both activation energies for Mn/Ag (70/30) (curves B and C) were about 2 kcal/mol, which indicated that the reactions were very rapid and the diffusion of reactants, probably CO, on the surface of the catalyst seemed to be rate determining. The rate of oxygen removal for the Mn catalyst increased with an increase in

the temperature to almost the same value as those observed for Mn/Ag (70/30) which were limited by diffusion. Although the exact rate of oxygen removal could not be evaluated for Mn/Ag (70/30), it is clear that the composite catalyst had much more labile and easily reducible lattice oxygen than the Mn catalyst.

As introduction of nitrogen on Mn/Ag (70/30) at 400°C caused the loss of lattice oxygen bonded to Ag (Fig. 5), the change in the valence states of Mn and Ag was investigated after the above procedure. The value of the MNN Auger peak of Ag was found to be 903.4 eV, which indicated that little change occurred in the valence of Ag, although oxygen bonded to Ag was lost (see Table 1). On the other hand chemical analysis indicated that the valence of Mn decreased from 3.2 to 2.8. If we assume that the state of Ag was seemingly still Ag_2O after loss of its lattice oxygen, the following change in the composition of the catalyst should have occurred,



The loss of oxygen based upon the above change corresponded to 93% of the lattice oxygen of Ag in the starting catalyst, $\text{MnO}_{1.6}(3/7)\text{AgO}_{0.5}$. This value agreed well with about an 80% loss of lattice oxygen bonded to Ag observed on an introduction of nitrogen at 400°C. (see Fig. 5) This fact shows that although the oxygen bonded to Ag was very active and was readily removed, the oxygen was in turn supplied from Mn and reduction of Mn occurred as a result. As Mn served as the oxygen supplier in this way, Ag retained its oxidized form during calcination, even at 400°C in air (see Table 1). When the proportion of Ag was too high (more than 50 mol%), Mn could not supply sufficient oxygen; thus reduction and aggregation of Ag became predominant.

From a consideration of the relation between oxidation activity of metal oxides and their heat of formation, the following characteristics of Mn and Ag are suggested

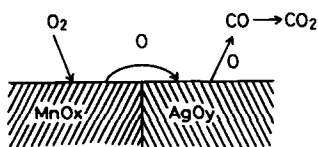
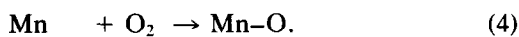
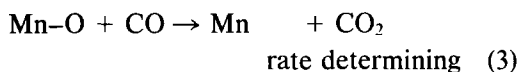
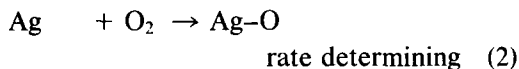


FIG. 7. Oxidation of CO by Mn/Ag catalyst.

(17). Interaction of Ag with oxygen is not strong and oxygen is readily removed. However, incorporation of oxygen by reduced Ag is difficult, and this step is rate determining in oxidation reactions. By contrast, reoxidation of reduced Mn is rapid and the rate determining step is the release of oxygen from Mn,



These characteristics of Ag and Mn provide an excellent cooperative action in the composite catalyst as shown in Fig. 7. The role of Ag is to oxidize CO, and the reoxidation of Ag is readily accomplished by the transfer of oxygen from Mn, thus eliminating the rather slow process of step (2). As reoxidation of Mn (step 4) is rapid, it serves as an oxygen reservoir and maintains Ag in the oxidized state, thus preventing the reduction of Ag to the metallic state, along with its subsequent aggregation. The present deduction that the reoxidation of the composite catalyst is not rate limiting is in agreement with the result that the reaction over Mn/Ag (70/30) was independent of oxygen pressure. The same rate dependence on oxygen pressure was obtained in the reaction over the Mn catalyst for which incorpora-

tion of oxygen (step 4) is not rate determining.

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