CHAPTER III

RESULTS AND DISCUSSION

3.1 Temperature for 50% Conversion ($T_{1/2}$) Tests

Figures 3.1, 3.4, 3.7, 3.10, 3.13, 3.18, and 3.21 showed the relation between temperature and %CO conversion for Ag, Mn, Co, Mn-Co (1:1), Ag-Mn (1:1), Ag-Co (1:1), and Ag-Mn-Co (2:1:1) catalysts, respectively. $T_{1/2}$ was obtained by determining temperature at 50% CO conversion. The lower $T_{1/2}$ shows the higher catalytic activity.

$T_{1/2}$ (See Tables 3.4 and 3.8), XRD (See Tables 3.1 and 3.5.), TGA (See Figures 3.3, 3.6, 3.9, 3.12, 3.15, 3.20, and 3.23), BET surface area (See Tables 3.2 and 3.6), and average pore radius (See Tables 3.3 and 3.7) showed that temperature and environmental condition were the crucial parameters in influencing catalytic performance. They affected changes in the material properties of the catalyst.

Table 3.1 Phase identification of transition metal oxide catalysts (Ag, Mn, Co, and Mn-Co (1:1) catalysts).

Catalyst	Unpretreated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C
Ag catalyst	Ag_2CO_3, Ag_2O	Ag_2CO_3 ↓, Ag_2O ↑	Ag	Ag
Mn catalyst	$MnCO_3$	$MnCO_3$	Mn_5O_8, $MnO_{1.88}$	$MnCO_3$
Co catalyst	$2CoCO_3.3Co(OH)_2.H_2O$	$2CoCO_3.3Co(OH)_2.H_2O$ ↓, Co3O4	Co_3O_4 ↑	Co_3O_4, Co
Mn-Co catalyst	$MnCO_3$, $2CoCO_3.3Co(OH)_2.H_2O$	$MnCO_3$, Co_3O_4	$MnCO_3$ ↓, Co_3O_4, $CoMnO_3$	$MnCO_3$, Co_3O_4

Table 3.2 BET surface area (m^2/g) of transition metal oxide catalysts (Ag, Mn, Co, and Mn-Co (1:1) catalysts).

Catalyst	Unpretreated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C
Ag catalyst	1.0560	1.1310	0.3224	0.3955
Mn catalyst	9.075	12.06	48.60	15.99
Co catalyst	133.40	107.70	22.39	69.04
Mn-Co catalyst	59.59	68.55	100.60	68.85

Table 3.3 Average pore radius (°A) of transition metal oxide catalysts (Ag, Mn, Co, and Mn-Co (1:1) catalysts).

Catalyst	Unpretreated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C
Ag catalyst	92.99	125.20	78.21	73.24
Mn catalyst	92.51	69.01	93.80	87.97
Co catalyst	70.03	78.72	263.2	118.6
Mn-Co catalyst	87.59	73.20	77.81	67.24

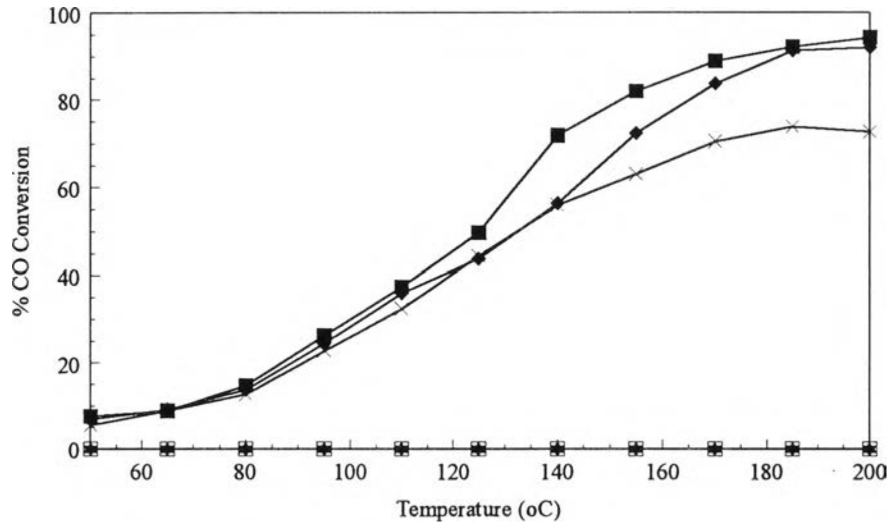

Figure 3.1 Temperature for 50% conversion of CO in the catalytic oxidation reaction over Ag catalysts: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C; (✱) catalyst calcined at 500°C; (□) catalyst after hydrogen reduction at 200°C; (x) catalyst humidified at 100°C.

Figure 3.2 showed that metallic Ag was formed by calcining at 500°C, because Ag_2O and Ag_2CO_3 were the thermally unstable above 300°C (See Figure 3.3). By using $T_{1/2}$ (See Figure 3.1) and XRD results, these showed that metallic Ag was the non-active species.

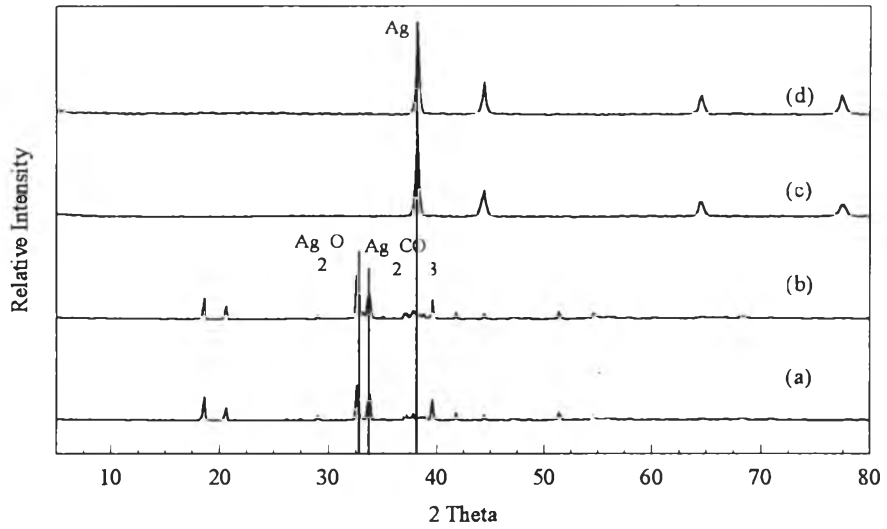

Figure 3.2 X-ray pattern for Ag catalysts: (a) unpretreated catalyst; (b) catalyst calcined at 200°C; (c) catalyst calcined at 500°C; (d) catalyst after hydrogen reduction at 200°C.

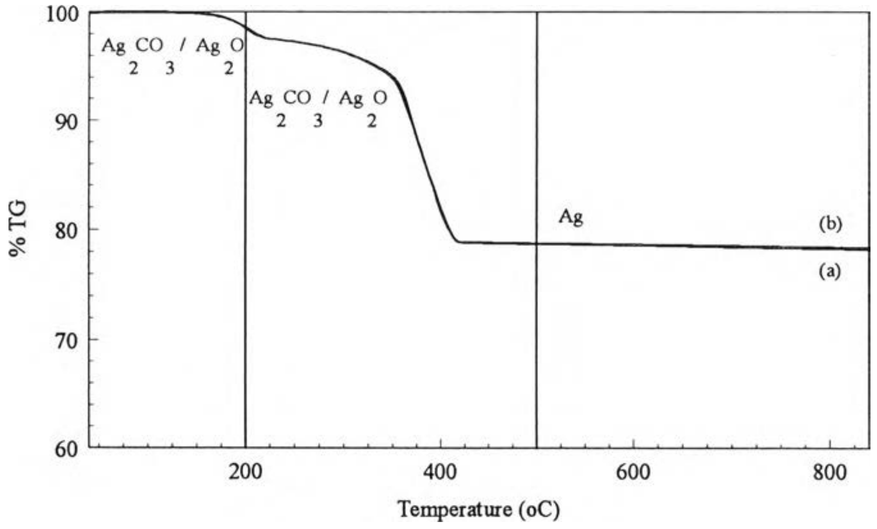

Figure 3.3 Thermogram for Ag catalysts: (a) nitrogen environment; (b) oxygen environment.

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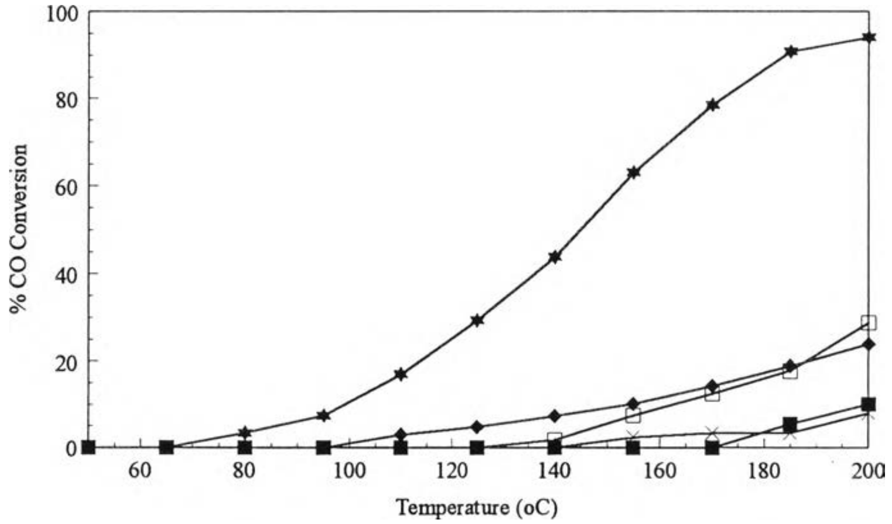

Figure 3.4 Temperature for 50% conversion of CO in the catalytic oxidation reaction over Mn catalysts: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C; (✱) catalyst calcined at 500°C; (□) catalyst after hydrogen reduction at 200°C; (x) catalyst humidified at 100°C.

Figures 3.4, 3.5, and 3.6 showed that non-active species $MnCO_3$ (low surface area, 9.075 m^2/g (See Table 3.2)) was changed to highly active manganese oxide species (high surface, 48.60 m^2/g (See Table 3.2)) when catalyst was calcined at temperature of 500°C.

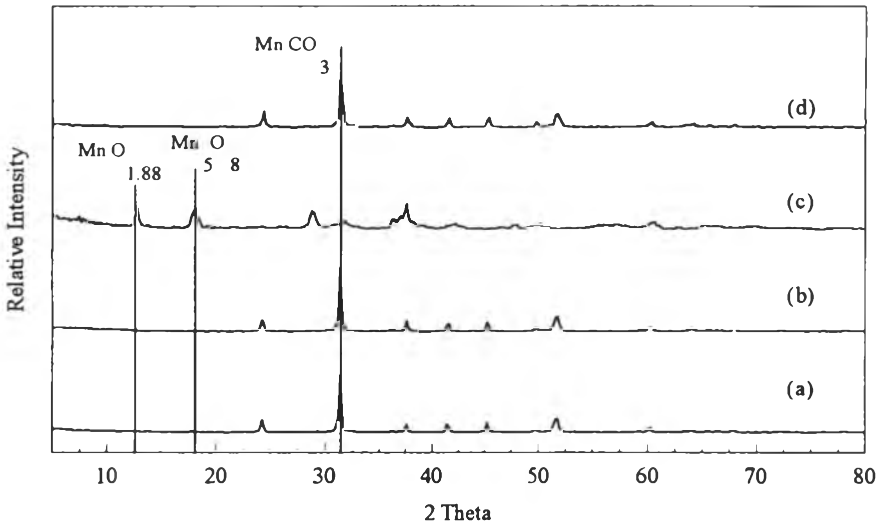

Figure 3.5 X-ray pattern for Mn catalysts: (a) unpretreated catalyst; (b) catalyst calcined at 200°C; (c) catalyst calcined at 500°C; (d) catalyst after hydrogen reduction at 200°C.

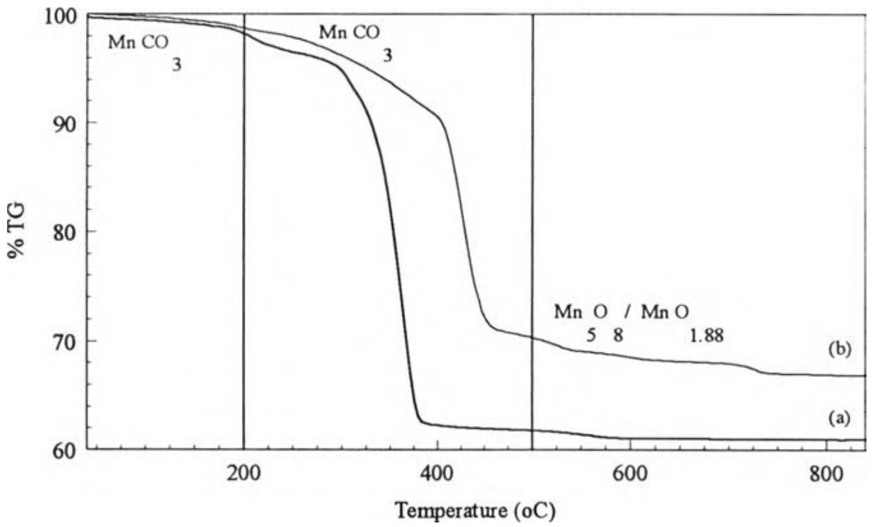

Figure 3.6 Thermogram for Mn catalysts: (a) nitrogen environment, (b) oxygen environment.

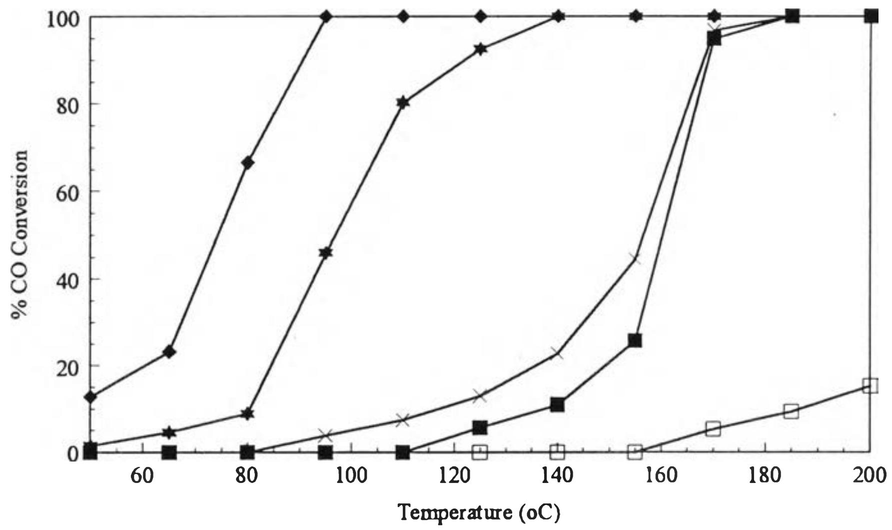

Figure 3.7 Temperature for 50% conversion of CO in the catalytic oxidation reaction over Co catalysts: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C; (✱) catalyst calcined at 500°C; (□) catalyst after hydrogen reduction at 200°C; (x) catalyst humidified at 100°C.

Because unpretreated Co catalyst had the small pore size (See Table 3.3), it was possible to occur water condensation in pores. This excess water molecules would hinder the reaction due to covering the pores of catalyst (thus “blocking” reaction sites). As it was shown in Figure 3.7, the catalytic activity of Co catalyst calcined at 200°C increased significantly in comparison to unpretreated Co catalyst due to a loss of some amount of moisture (See Figure 3.9) from pores blocked the reaction sites. Unlike catalyst calcined at 200°C, a loss of surface area after calcination at 500°C affected the decrease in catalytic activity of Co catalyst as shown in Table 3.2.

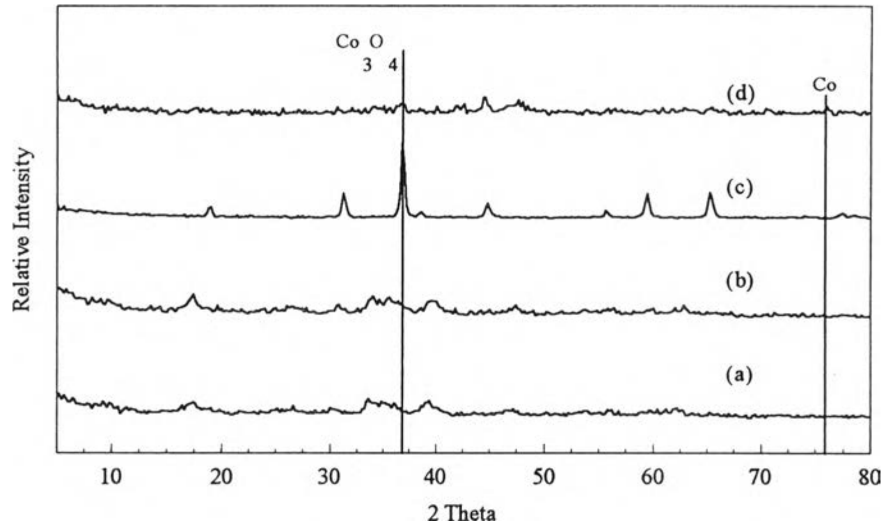

Figure 3.8 X-ray pattern for Co catalysts: (a) unpretreated catalyst; (b) catalyst calcined at 200°C; (c) catalyst calcined at 500°C; (d) catalyst after hydrogen reduction at 200°C.

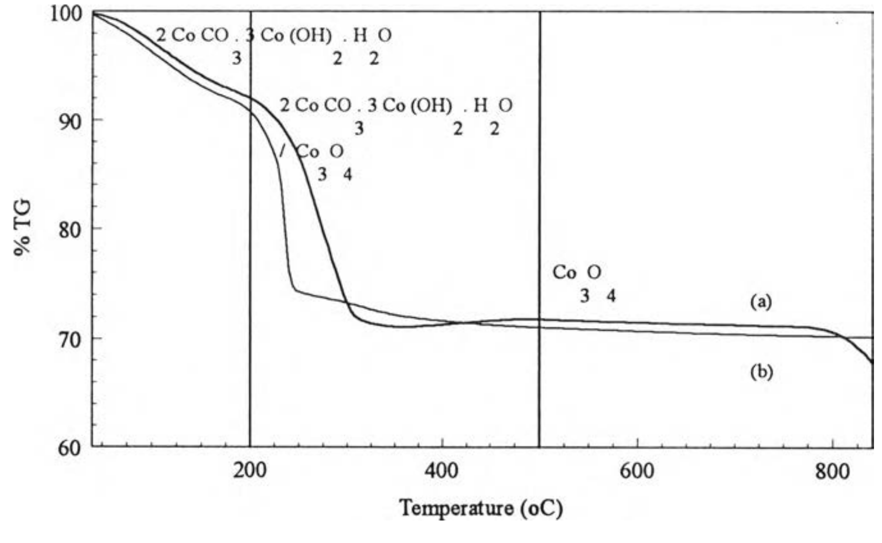

Figure 3.9 Thermogram for Co catalysts: (a) nitrogen environment, (b) oxygen environment.

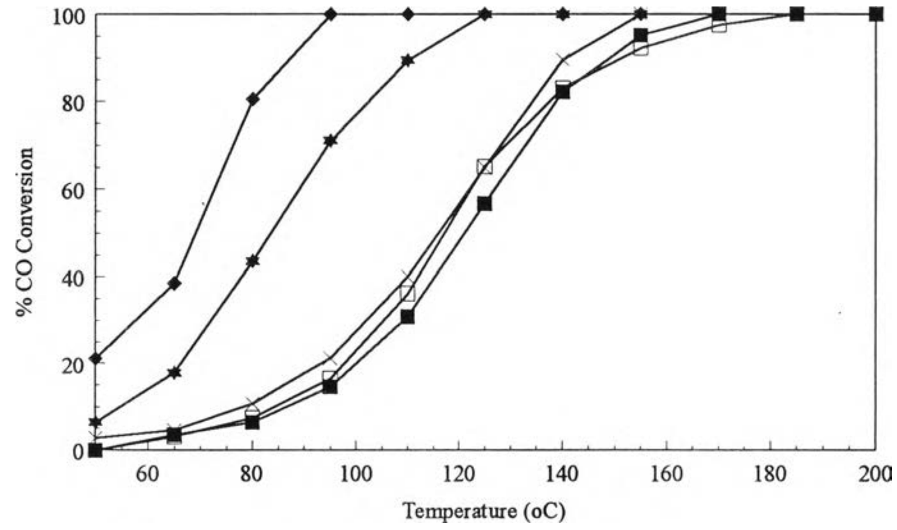

Figure 3.10 Temperature for 50% conversion of CO in the catalytic oxidation reaction over Mn-Co (1:1) catalysts: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C; (✶) catalyst calcined at 500°C; (□) catalyst after hydrogen reduction at 200°C; (x) catalyst humidified 100°C.

Table 3.4 Temperature for 50% conversion ($T_{1/2}$) of transition metal oxide catalysts (Ag, Mn, Co, and Mn-Co (1:1) catalysts) with various pretreatment methods.

Catalyst	Unpre-treated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C	Catalyst humidified at 100°C
Ag catalyst	**125**	133	*	*	132
Mn catalyst	*	*	**145**	*	*
Co catalyst	161	**74**	96	*	157
Mn-Co catalyst	121	**69**	84	117	116

*** : never converted to 50% conversion**

Table 3.4 summarized $T_{1/2}$ for Ag, Mn, Co, and Mn-Co catalysts at different pretreatment methods. It showed that combined Mn and Co catalyst had the higher catalytic activity compared with single transition metal catalysts, because all Mn-Co catalysts had very high surface area (See Table 3.2) and consisted of two different species which had different roles of CO and O_2 adsorption and different heats of formation (Haruta and Sano, 1983)). Moisture still had a strong influence on the decrease in activity as shown in Figure 3.10; therefore, the unpretreated catalyst had a lower activity compared with catalyst calcined at 200°C. Excess water would hinder the reaction, since Mn-Co catalyst had a Co component with small pores.

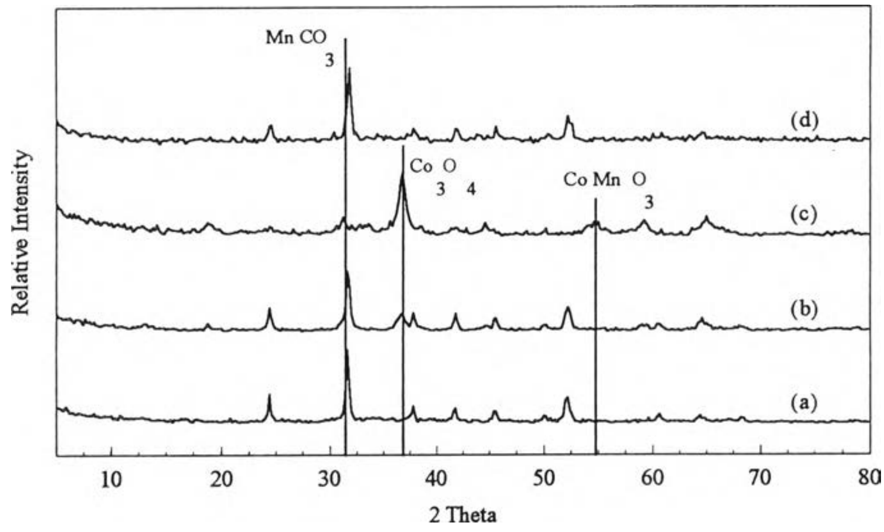

Figure 3.11 X-ray pattern for Mn-Co catalysts: (a) unpretreated catalyst; (b) catalyst calcined at 200°C; (c) catalyst calcined at 500°C; (d) catalyst after hydrogen reduction at 200°C.

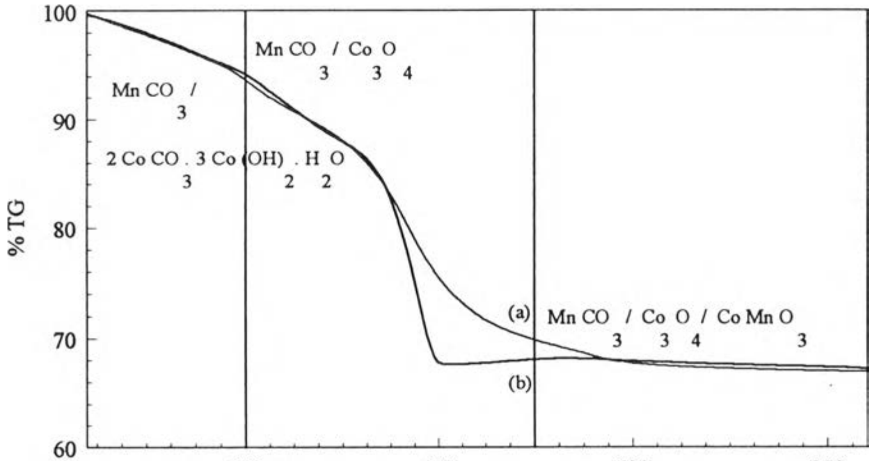

Figure 3.12 Thermogram for Mn-Co catalysts: (a) nitrogen environment, (b) oxygen environment.

Base metal (Mn, Co) oxide enhanced the thermal stability of Ag catalyst (Thomas and Thomas, 1967); therefore, the reducible metal oxide supported silver catalysts were synthesized by coprecipitation method to develop higher performance and more stability.

Table 3.5 Phase identification of transition metal oxide supported silver catalysts (Ag-Mn (1:1), Ag-Co (1:1), and Ag-Mn-Co (2:1:1) catalysts).

Catalyst	Unpretreated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C
Ag-Mn catalyst	Ag, Ag_2O, Mn_3O_4, $AgMn_2O_4$	Ag ↓, Ag_2O, Mn_3O_4 ↓, $AgMn_2O_4$ ↑	Ag ↓, Ag_2O, Mn_3O_4 ↓, $AgMn_2O_4$ ↑	Ag, non-crystalline substance
Ag-Co catalyst	Ag. $AgCoO_2$	Ag, $AgCoO_2$	Ag, $AgCoO_2$	Ag, non-crystalline substance
Ag-Mn-Co catalyst	Ag, $CoMn_2O_4$	Ag, $CoMn_2O_4$	Ag, $CoMn_2O_4$	Ag, non-crystalline substance

Table 3.6 BET surface area (m^2/g) of transition metal oxide supported silver catalysts (Ag-Mn (1:1), Ag-Co (1:1), and Ag-Mn-Co (2:1:1) catalysts).

Catalyst	Unpretreated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C
Ag-Mn catalyst	29.15	28.38	16.47	24.75
Ag-Co catalyst	65.75	63.00	16.73	10.81
Ag-Mn-Co catalyst	57.48	56.40	44.68	45.53

Table 3.7 Average pore radius (°A) of transition metal oxide supported silver catalysts (Ag-Mn (1:1), Ag-Co (1:1), and Ag-Mn-Co (2:1:1) catalysts).

Catalyst	Unpretreated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C
Ag-Mn catalyst	167.50	236.70	212.80	232.20
Ag-Co catalyst	84.74	105.70	277.30	260.40
Ag-Mn-Co catalyst	95.14	97.50	109.10	113.50

Table 3.5 showed phases in the reducible metal oxide supported silver catalysts (Ag-Mn, Ag-Co, and Ag-Mn-Co catalysts). Unlike Ag catalyst, no metallic Ag was formed or sintered upon calcination, because the amount of composite oxide (such as $AgMn_2O_4$, $AgCoO_2$) increased upon raising calcination temperature.

Although the amount of non-active metallic Ag decreased upon calcination, it cannot be postulated that the catalytic activities increased. The catalytic performance depended on many factors, such as phase (See Table 3.5), surface area (See Table 3.6), and pore size (See Figure 3.7).

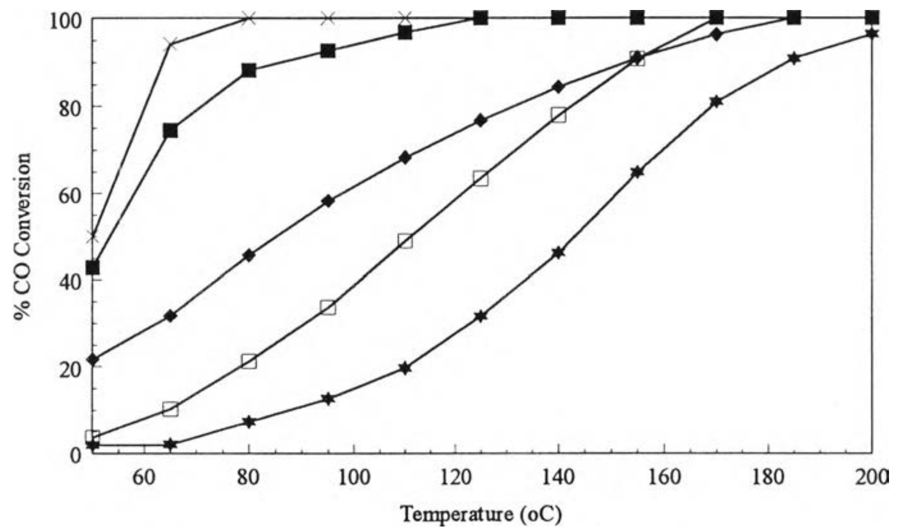

Figure 3.13 Temperature for 50% conversion of CO in the catalytic oxidation reaction over Ag-Mn (1:1) catalysts: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C; (✶) catalyst calcined at 500°C; (□) catalyst after hydrogen reduction at 200°C; (x) catalyst humidified at 100°C.

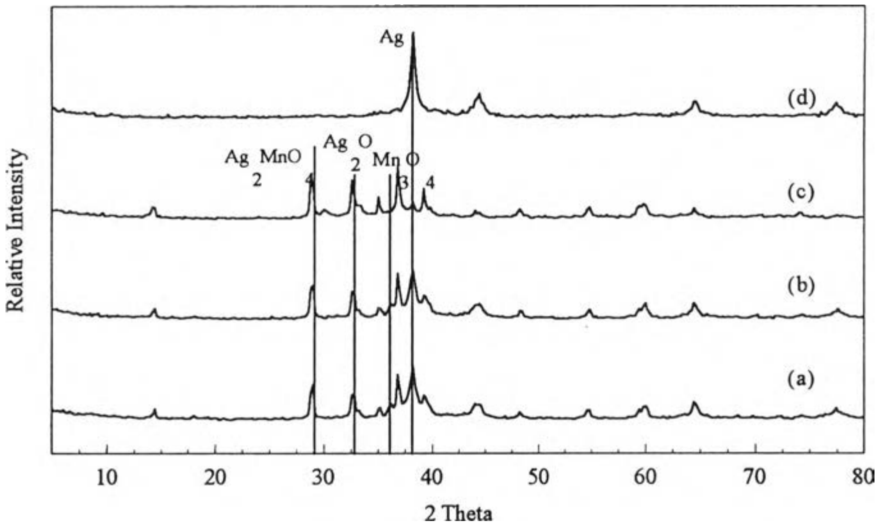

Figure 3.14 X-ray pattern for Ag-Mn (1:1) catalysts: (a) unpretreated catalyst; (b) catalyst calcined at 200°C; (c) catalyst calcined at 500°C; (d) catalyst after hydrogen reduction at 200°C.

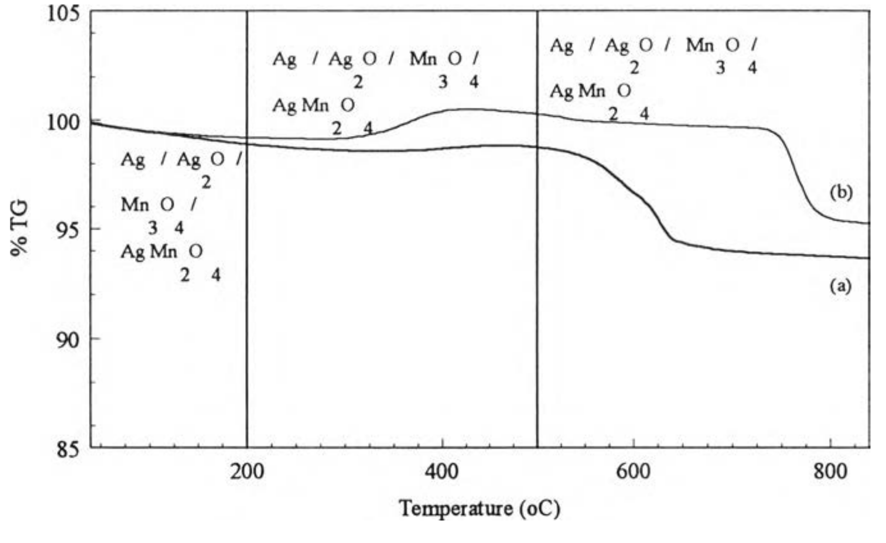

Figure 3.15 Thermogram for Ag-Mn (1:1) catalysts: (a) nitrogen environment, (b) oxygen environment.

Moisture in the catalyst can be eliminated by heating over 100°C as shown in Figure 3.15, so catalysts calcined at 200°C had a small amount of moisture content. Figure 3.13 showed that moisture strongly affected the catalytic activity of Ag-Mn catalyst, because the humidified catalyst had the highest activity as shown in Figure 3.13.

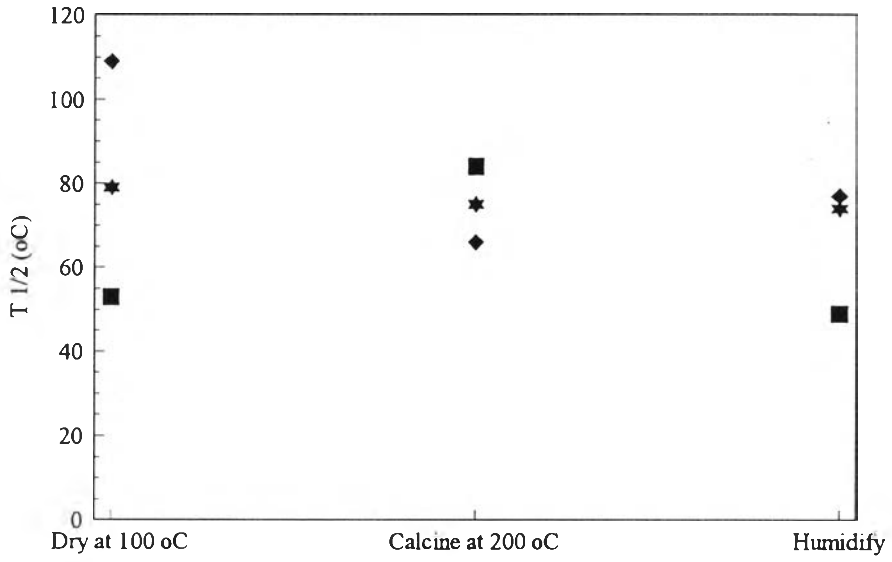

Figure 3.16 Temperature for 50% conversion of CO in the catalytic oxidation reaction over reducible metal oxide supported silver catalysts: (■) Ag-Mn catalyst (1:1); (◆) Ag-Co catalyst (1:1); (✶) Ag-Mn-Co (2:1:1) catalyst.

Catalysts calcined at 200°C had lower moisture content compared with unpretreated catalysts (See Figure 3.15, 3.20, and 3.23), but we can increase the moisture contents of catalysts calcined at 200°C to the same level as unpretreated catalysts by humidification pretreatment at 100°C for 1 hour. Figure 3.16 showed that the activity of Ag-Mn catalyst calcined at 200°C increased after humidification method. This result confirmed that the moisture affected enhancing the catalytic activity of Ag-Mn catalyst.

The $AgMn_2O_4$ content increased, and metallic Ag and manganese oxide contents decreased upon calcination at 500°C as shown in Figure 3.14. These results were possible to changes of metallic Ag and manganese oxide to $AgMn_2O_4$ species upon heating. The amount of active species, manganese oxide, decreased upon calcination as shown in Table 3.5; thus, the activity of catalyst calcined at 500°C decreased notably.

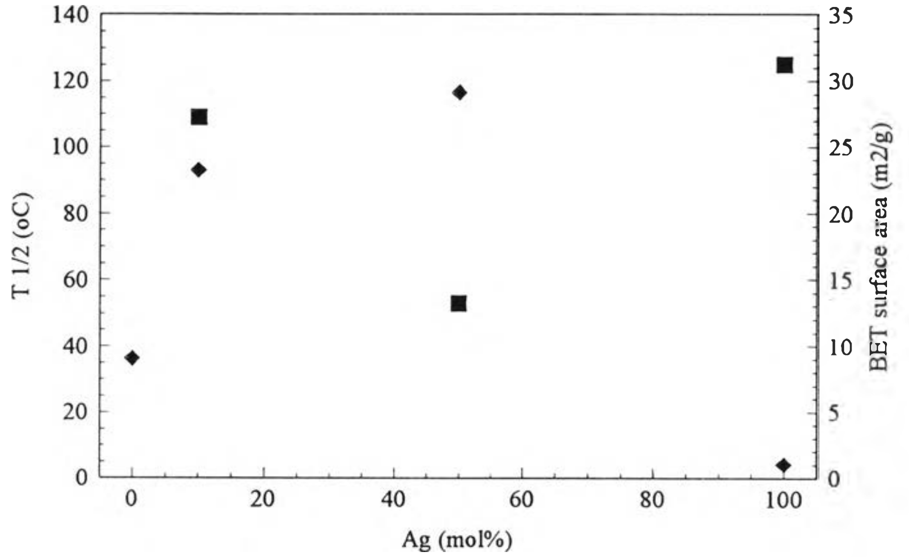

Figure 3.17 Oxidation of CO by Ag/Mn catalysts: (■) temperature for 50% conversion; (◆) BET surface area.

From Figure 3.17, composite catalysts (Ag and Mn) had much superior performance to the pure Mn and Ag catalysts over the entire temperature range, since the combination of Ag and Mn components enhanced the surface area of pure Ag or Mn catalysts.

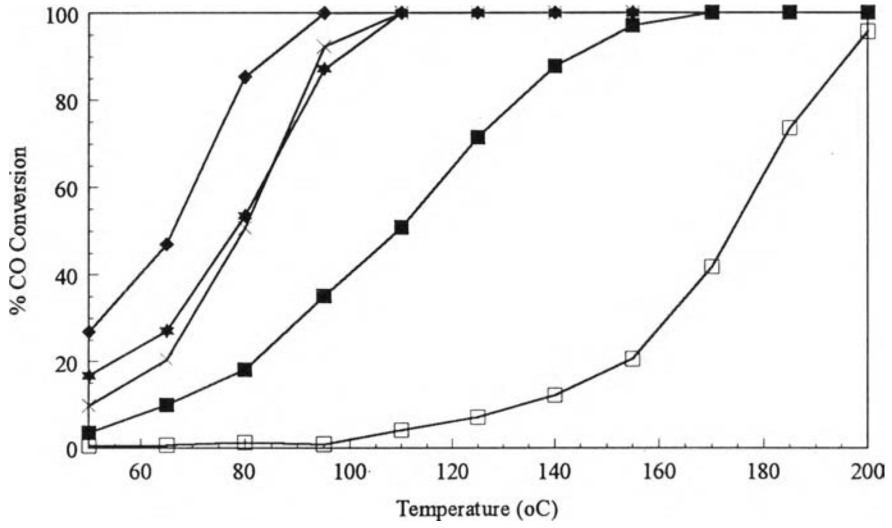

Figure 3.18 Temperature for 50% conversion of CO in the catalytic oxidation reaction over Ag-Co (1:1) catalysts: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C; (✱) catalyst calcined at 500°C; (☐) catalyst after hydrogen reduction at 200°C; (x) catalyst humidified at 100°C.

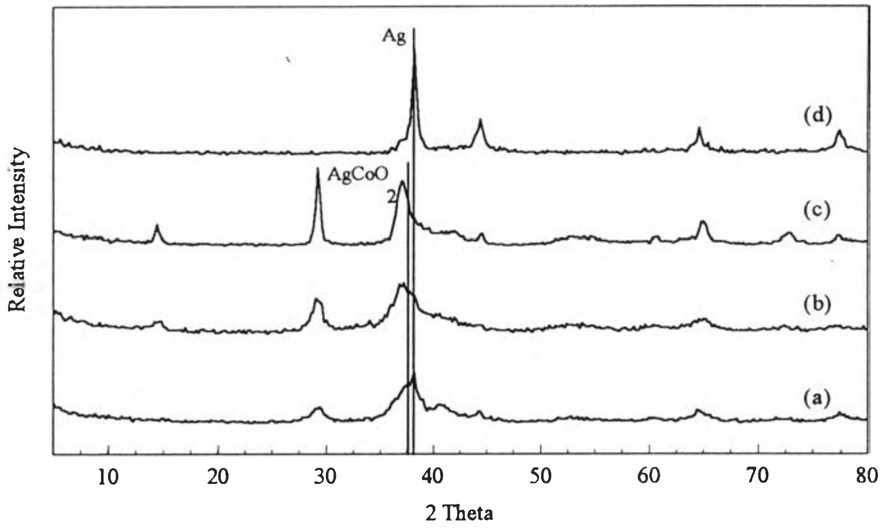

Figure 3.19 X-ray pattern for Ag-Co (1:1) catalysts: (a) unpretreated catalyst; (b) catalyst calcined at 200°C; (c) catalyst calcined at 500°C; (d) catalyst after hydrogen reduction at 200°C.

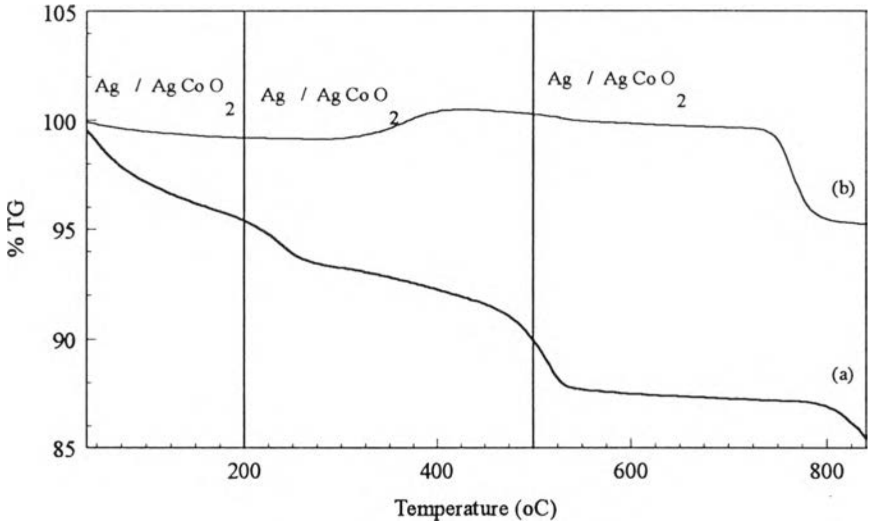

Figure 3.20 Thermogram for Ag-Co (1:1) catalysts: (a) nitrogen environment, (b) oxygen environment.

The unpretreated Ag-Co catalyst had the smallest pore size (See Table 3.7); therefore, excess water molecules may hinder the reaction by covering the catalyst. Since some amount of moisture lost from pores upon heating to 200°C (See Figure 3.20), pore size of Ag-Co catalyst increased (See Table 3.7). Increase in pore size enhanced the catalytic activity of Ag-Co catalyst and it was confirmed by humidification Ag-Co catalyst. To increase the moisture content affected decreased in the activity (See Figure 3.16).

From Figure 3.19, increase in calcination temperature affected decrease in non-active metallic Ag content and increase in $AgCoO_2$ species, which may have been the active species, but the catalytic activity did not increase as shown in Table 3.6. This was significantly caused by the loss of surface area (decrease from 65.75 m^2/g to 16.73 m^2/g) at 500°C (See Table 3.6).

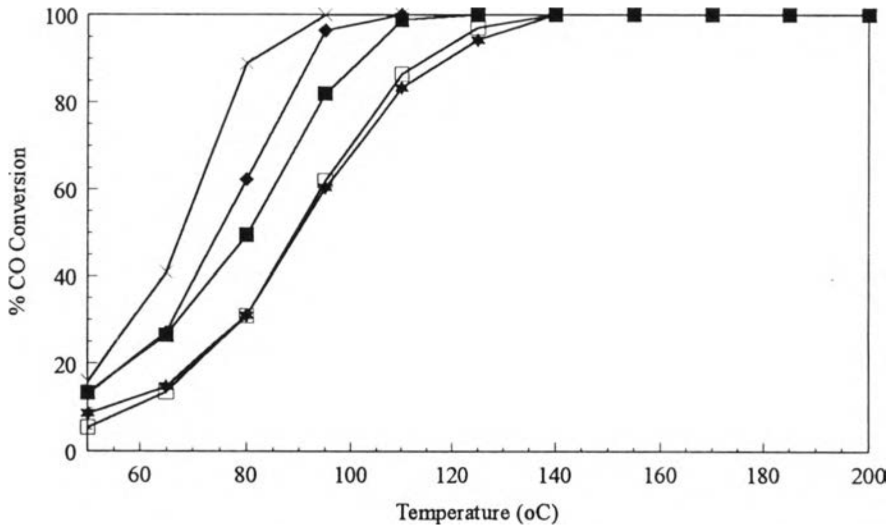

Figure 3.21 Temperature for 50% conversion of CO in the catalytic oxidation reaction over Ag-Mn-Co (2:1:1) catalysts: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C; (✱) catalyst calcined at 500°C; (□) catalyst after hydrogen reduction at 200°C; (x) catalyst humidified at 100°C.

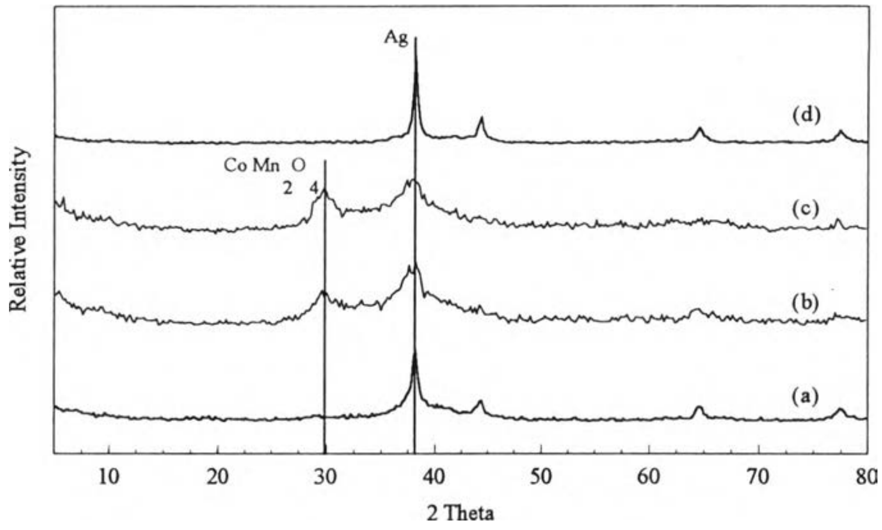

Figure 3.22 X-ray pattern for Ag-Mn-Co (2:1:1) catalysts: (a) unpretreated catalyst; (b) catalyst calcined at 200°C; (c) catalyst calcined at 500°C; (d) catalyst after hydrogen reduction at 200°C.

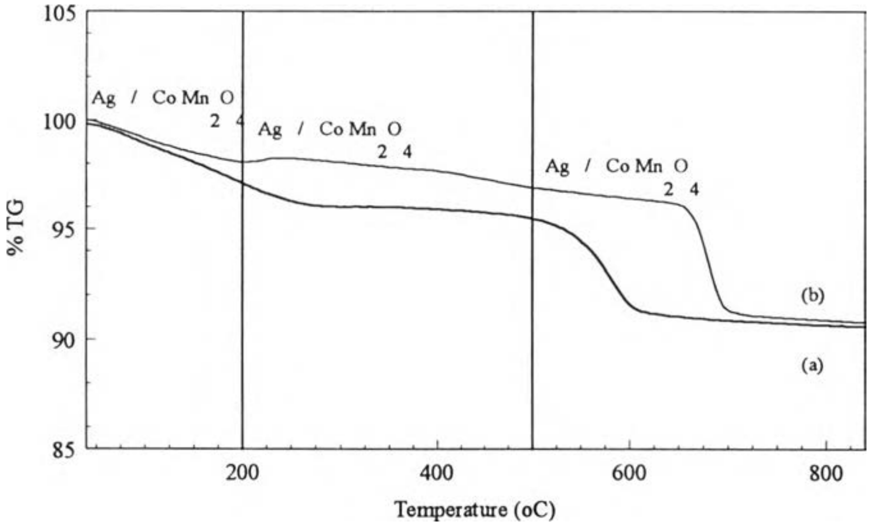

Figure 3.23 Thermogram for Ag-Mn-Co (2:1:1) catalysts: (a) nitrogen environment, (b) oxygen environment.

Ag-Mn-Co catalyst was the most tolerant to temperature, reduction, and moisture, because the temperature for 50% conversion (See Figure 3.21), the surface area (See Table 3.6), and the pore size (See Table 3.7) of Ag-Mn-Co catalyst had the smallest changes compared to other catalysts. Moreover, higher calcination temperature resulted in increase in amount of non-active $CoMn_2O_4$ as shown in Figures 3.21 and 3.22. Therefore, unpretreated catalyst had higher activity than other pretreated catalysts because of the lowest amount of non-active $CoMn_2O_4$.

Table 3.8 Temperature for 50% conversion ($T_{1/2}$) of transition metal oxide supported silver catalysts (Ag-Mn (1:1), Ag-Co (1:1), and Ag-Mn-Co (2:1:1) catalysts) with various pretreatment methods.

Catalyst	Unpre-treated catalyst	Catalyst calcined at 200°C	Catalyst calcined at 500°C	Catalyst after hydrogen reduction at 200°C	Catalyst humidified at 100°C
Ag-Mn catalyst	<u>53</u>	84	144	111	50
Ag-Co catalyst	109	<u>66</u>	79	174	80
Ag-Mn-Co catalyst	79	<u>75</u>	90	89	68

Table 3.8 summarized temperature for 50% conversion of reducible metal oxide supported silver catalysts. It showed that the addition of Ag component to base metal (Mn, Co) component(s) enhanced the catalytic performance. This high activity was caused by differences in the active

species which had different heats of formations (or the affinities of both base metal and silver components were different) (Haruta and Sano, 1983).

TGA of reducible metal oxide supported silver catalysts in Figures 3.15, 3.20, and 3.23 as compared with TGA of pure silver catalyst (See Figure 3.3) showed that the reducible metal oxide supported silver catalysts had little changes in mass loss upon heating. Their changes were below 15 percents; hence, it indicated that the addition of base transition metal (Mn, Co) oxides enhanced the thermal stability.

3.2 Deactivation Tests

Comparing the temperature for 50% conversion of all catalysts as shown in Tables 3.4 and 3.8. Ag-Mn catalyst was the most active catalyst; therefore, the deactivation scenarios of Ag-Mn catalyst were investigated by the deactivation tests.

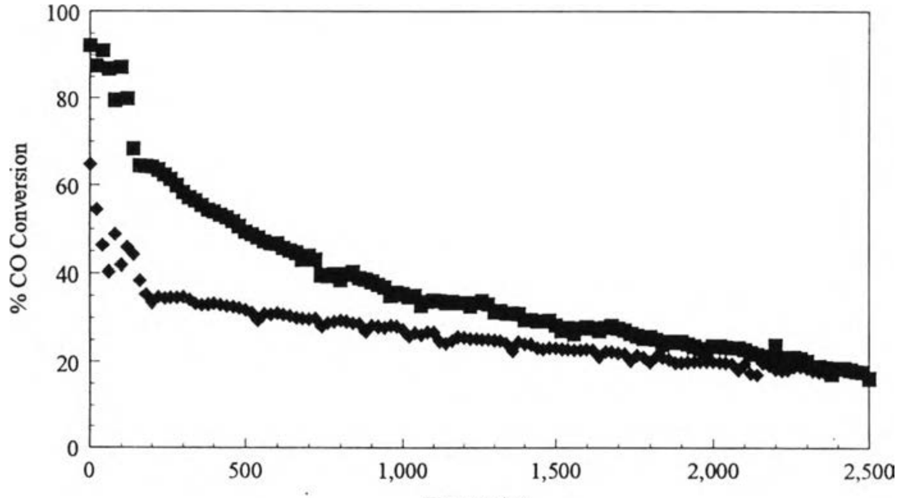

Figure 3.24 Deactivation tests for Ag-Mn (1:1) catalyst: (■) unpretreated catalyst; (◆) catalyst calcined at 200°C.

It can be observed from Figure 3.24 that the catalysts decayed rapidly in their activity during the first 500 minutes and slowly after 500 minutes. This was probably due to the losses of moisture and oxygen from the structure during first 500 minutes. The activity of unpretreated catalyst and catalyst calcined at 200°C reached to the same level after 2,500 minutes, since the moisture and oxygen contents in both catalysts should loss to quite the same level during the run.

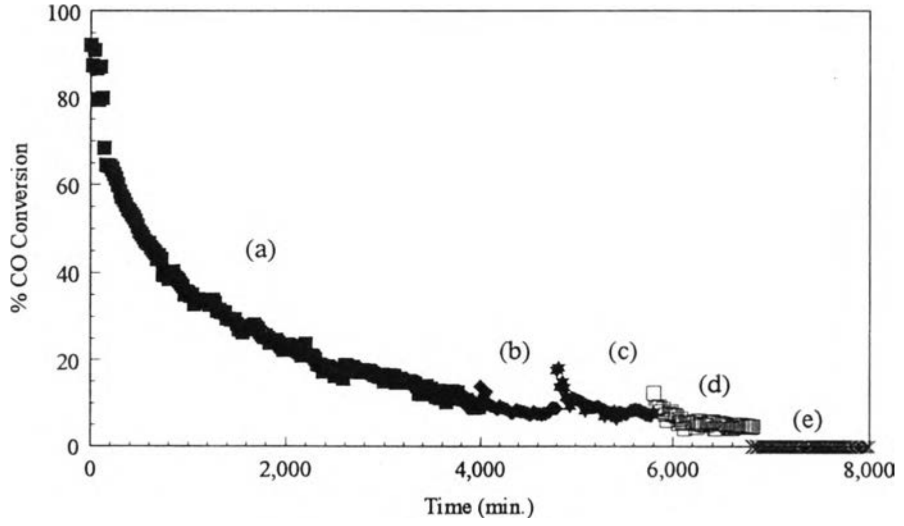

Figure 3.25 Deactivation tests for Ag-Mn (1:1) catalyst with various treatments: (a) no pretreatment; (b) humidification treatment at 100°C; (c) oxidation treatment at 200°C; (d) oxidation treatment at 200°C with moist gas; (e) both hydrogen reduction and oxidation treatment.

However, catalyst decayed continuously after 2,500 minutes as shown in Figure 3.25. This showed that there were the other important effects on the deactivation. They were possible to agglomerate of active silver oxide species and decrease in the active manganese oxide species.

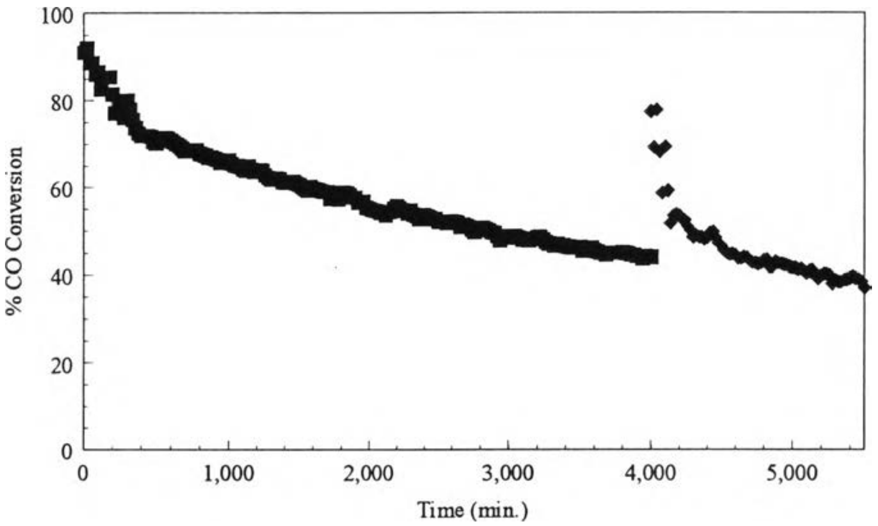

Figure 3.27 Deactivation tests for Ag-Mn (1:1) catalyst (100 mg): (■) before oxygen storage for 10 days; (◆) after oxygen storage for 10 days.

The amount of manganese oxide species decreased upon reaction, because it was possible to strongly adsorb of CO_2 (after CO reacted with O_2) on manganese oxide to form carbonate material (Thomas and Thomas, 1967). Figure 3.27 proved that the deactivation phenomena occurred when CO reacted with O_2 to form poison strongly adsorbed CO_2. If CO_2 was not present due to no CO oxidation reaction, the catalyst was not deactivated.

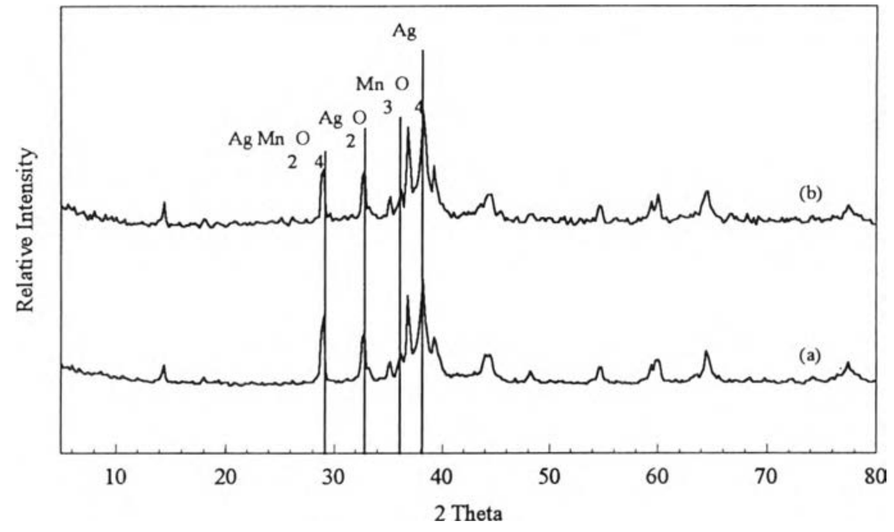

Figure 3.26 X-ray pattern for Ag-Mn (1:1) catalysts: (a) unreacted catalyst; (b) reacted catalyst for 4,000 minutes.

Figure 3.26 provided the glancing angle and the width of the peak angular of X-ray diffraction pattern of unreacted and reacted Ag-Mn catalysts. With these two parameters, the mean crystallite diameter of Ag_2O was calculated by Scherrer equation (Baiker, 1985) as shown in Table 3.9.

Table 3.9 Mean crystallite diameter (°A) of Ag_2O from Scherrer equation.

Ag-Mn catalyst	Mean crystallite diameter (°A) of Ag_2O from Scherrer equation
Fresh catalyst	259.835
Reacted catalyst for 4,000 minutes	353.795

Table 3.9 showed the increase in crystallite size of active Ag_2O species upon reaction. This proved that silver oxide was sintered; so the performance and the surface area of reacted Ag-Mn catalyst decreased to 10 and 23.41 m^2/g upon reaction, respectively.

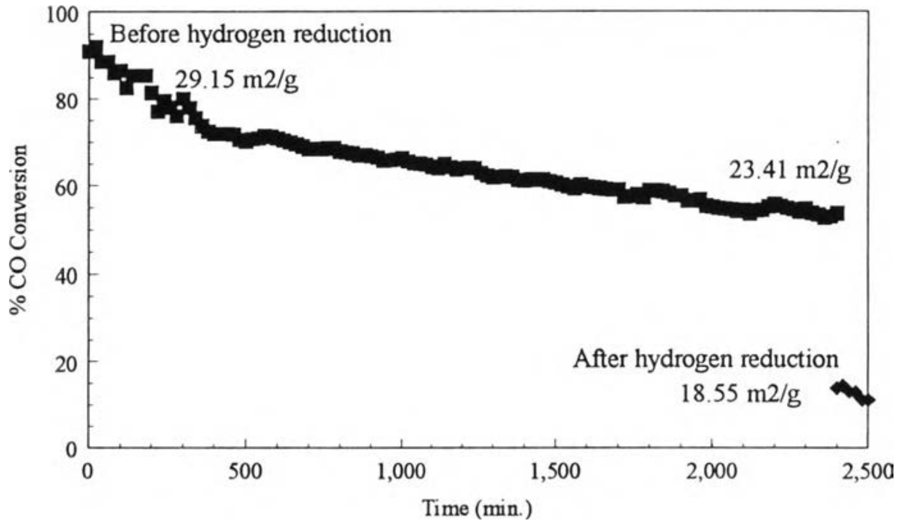

Figure 3.28 Deactivation tests for Ag-Mn (1:1) catalyst (100 mg): (■) before hydrogen reduction at 200°C for 1 hour; (◆) after hydrogen reduction at 200 °C for 1 hour.

Since silver oxide and manganese oxide were the active species as shown in temperature for 50% conversion results. If the amount of these two active sites decreased upon reaction, the performance had to decreased too. It was confirmed by hydrogen reduction at 200^{0}C as shown in Figure 3.28 that the activity of reduced catalyst decreased considerably because of phase changes of metallic oxide species to non-active metallic species (See Figure 3.29).

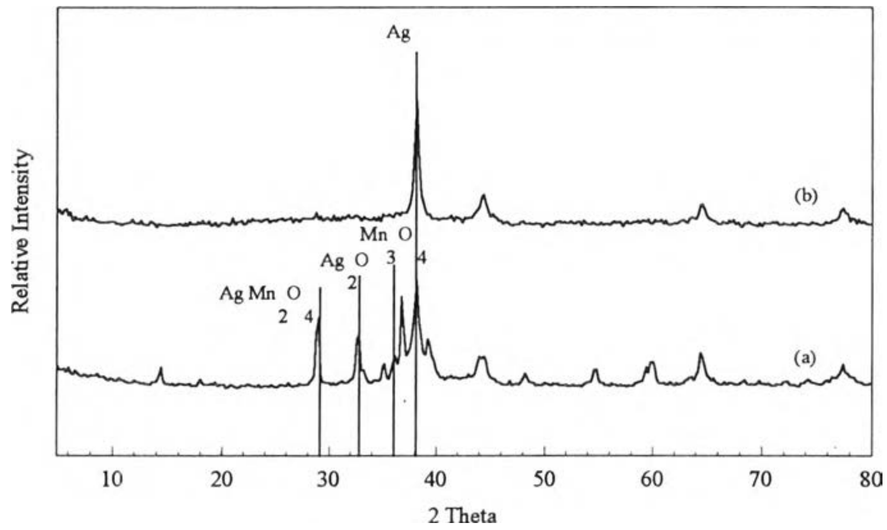

Figure 3.29 X-ray pattern for Ag-Mn (1:1) catalysts (100 mg): (a) before hydrogen reduction at 200°C for 1 hour; (b) after hydrogen reduction at 200°C for 1 hour.

We found that this deactivation was the irreversible process, because the regeneration tests (See Figure 3.25) showed that moisture and oxygen had little effects on an increase in activity of deactivated catalyst. The catalytic activity was never fully restored by humidification or oxidation treatments.