

CHAPTER IV

RESULTS AND DISCUSSTION

4.1 Catalytic Activity Tests

Based on the $T_{1/2}$ results, illustrated in Table 4.1, silver oxide catalysts were conducted the catalytic activity containing 0.1, 1 and 5 percent silver, 20 percent manganese and 80 percent cobalt oxides as a function of time at 50 and 40 °C. The results are shown in Figures 4.1 and 4.2. The activity of the catalysts increases with the silver loading; however, the change with loading is not linear or very dramatic. All catalysts have almost 100 percent conversion at 50 °C which decreases by a factor of two when the temperature is reduced to 40 °C. The relative decay in activity is also inversely proportional to the metal loading. It is observed that the five percent silver catalyst has the least decrease in activity. The conversion of the 0.1 percent silver catalyst decreases by 30 percent of its original activity after 10,000 minutes on stream; in comparison the activity of the five percent silver catalyst has decreased by 75 percent of its initial value. The one percent silver catalyst is intermediate. Along with lower initial activity, reduction of the reactor temperature to 40 °C results in faster activity decay for all the catalysts, even though the general shape of the curves is the same as the 50 °C data. This increased rate of decay may be due to accumulation of inactive species on the catalyst surface. The decay rate of the catalysts appears to be slower than the rates observed previously testing for 50 percent silver, or five percent gold catalysts conducted with one percent carbon monoxide containing feed stream (Srivannavit, S., M.S. thesis, the Petroleum and Petrochemical College, 1996 and Sze, C., Ph.D dissertation, the

Table 4.1 Temperature for 50% Conversion of Silver Oxides Catalysts

Catalysts	Catalysts dried at 100 °C	Catalysts calcined at 200 °C	Catalysts calcined at 300 °C
0.1%Ag99.9%Co	110	80	74
0.1%Ag99.9%Mn	170	145	151
0.1%Ag89.9%Co10%Mn	75	53	59
0.1%Ag80%Co19.9%Mn	70	<u>47</u>	55
0.1%Ag69.9%Co30%Mn	76	55	61
0.1%Ag49.95%Co49.95%Mn	85	68	73
0.1%Ag30%Co69.9%Mn	155	110	108
0.1%Ag10%Co89.9%Mn	160	115	110

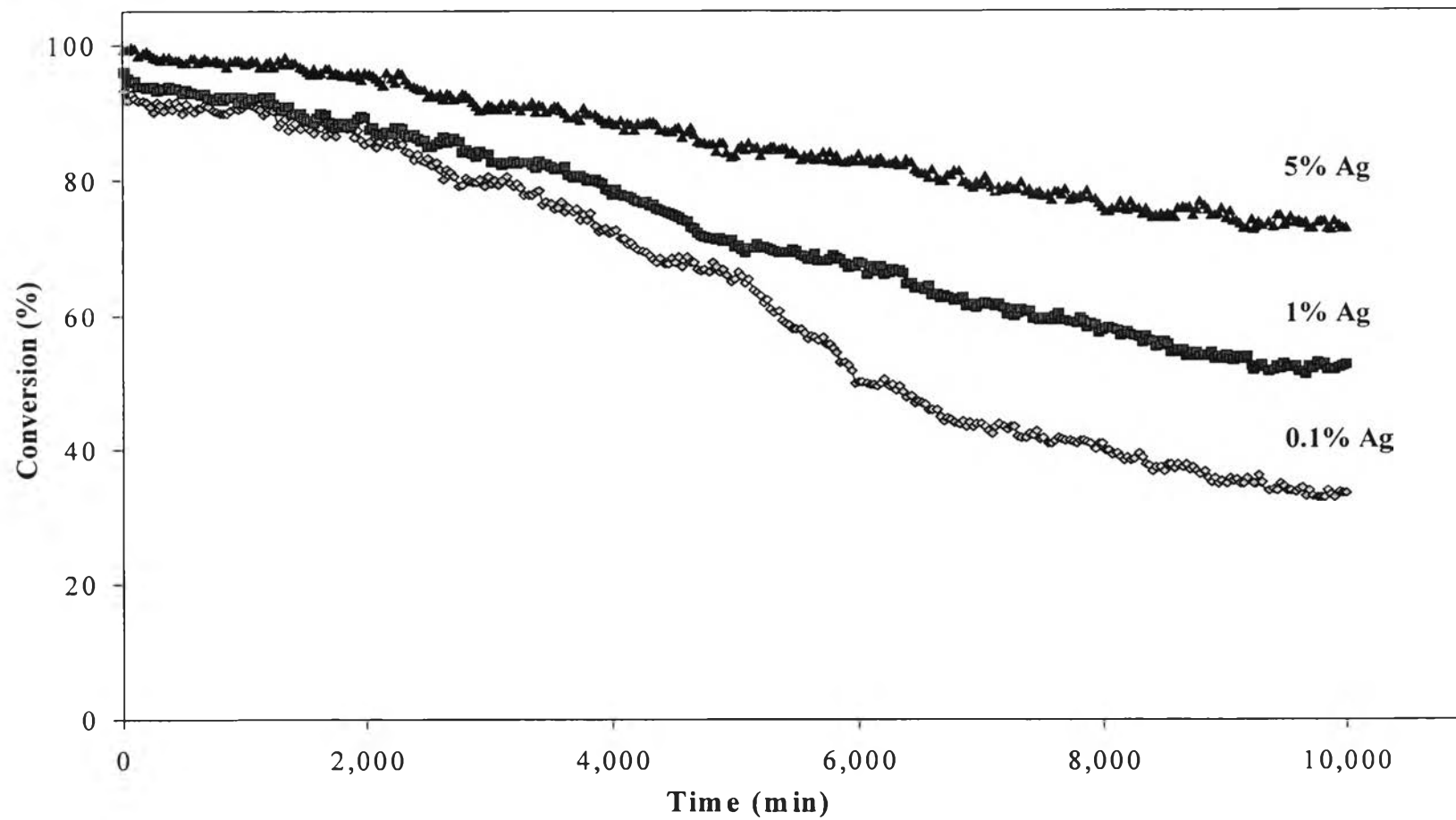


Figure 4.1 Deactivation Tests of Silver Oxide Catalysts at 50 °C.

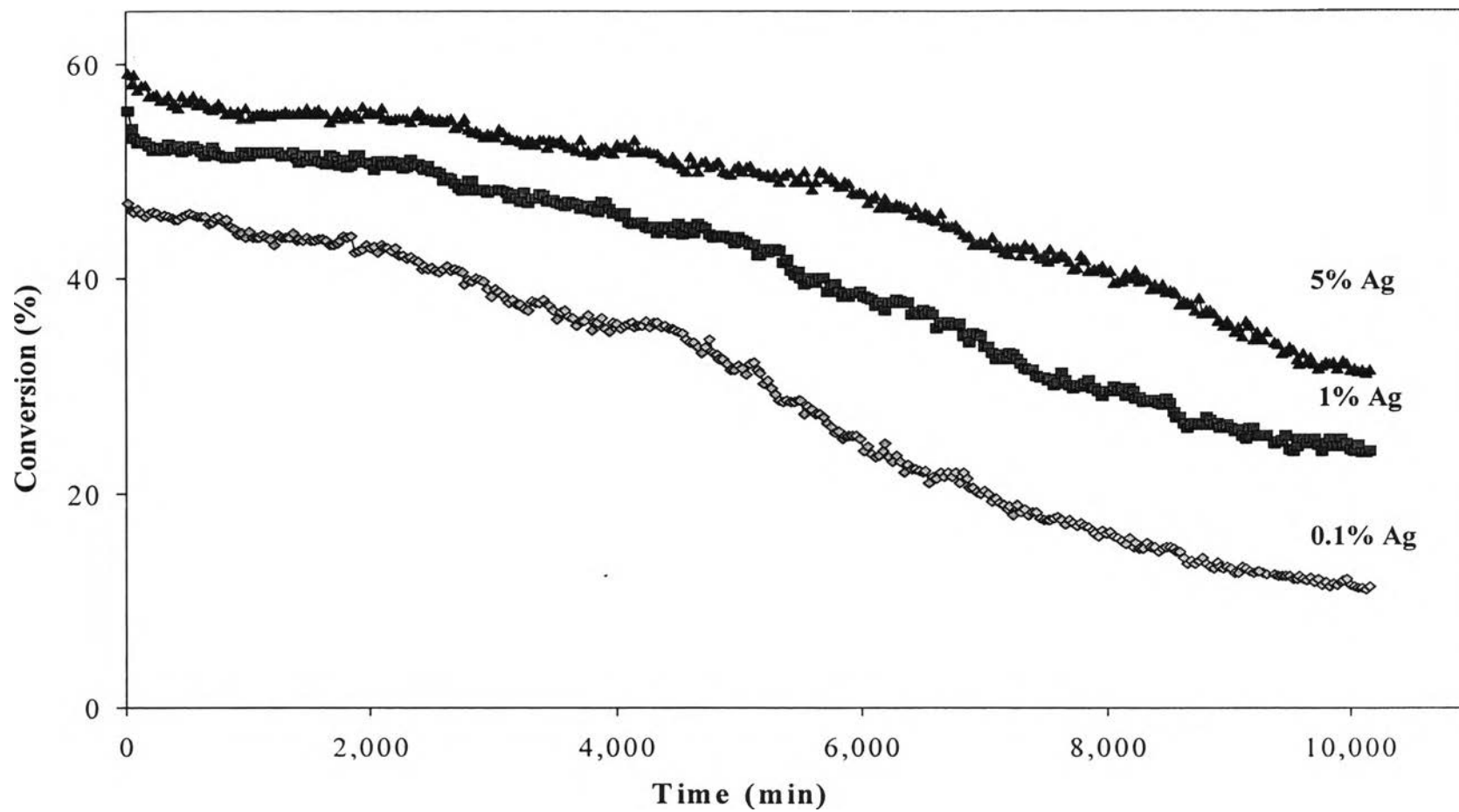


Figure 4.2 Deactivation Tests of Silver Oxide Catalysts at 40 °C.

University of Michigan, 1995). The difference may be due to desorption of the carbon dioxide formed or the formation of unreactive carbonates when carbon dioxide cannot desorb fast enough.

Figure 4.3 shows the effect of pretreatment on the activity of one percent silver loading catalysts. The catalyst oxidized at 200 °C has the highest activity. The conversion curve has two distinct regions. An initial high activity period is last slightly more than 1,000 minutes. During this time the conversion of the catalyst decreases from 90 to 52 percent. The second region is above 1,500 minutes and is characterized by a much slower decay in activity going from 52 to 35 percent in 10,000 minutes. In contrast the air calcined catalyst does not exhibit a long initial high activity period; only the slow decay regime is seen. The catalyst that was exposed to a humid reactant mixture by bubbling the helium through water at room temperature is initially almost dead. However, its activity keeps increasing and after about 1,800 minutes on stream which the activity goes through a transition and increases by a factor of five in a period of five to ten minutes. It was observed that the initial low level of activity and the jump in activity are due to starting with a catalyst which may have had water condense in its pores during the humidification pretreatment. The activity jumps to a higher level as soon as all of the water is evaporated from the pores. The decay properties of this catalyst are similar to the oxidized catalyst. The hydrogen reduced catalyst has high initial activity which decays in about 1,000 minutes and transitions into the long term decay period. The overall shape of the activity curve of this catalyst is rather similar to the high activity oxygen pretreated catalyst's curve. However, its activity in the slow decay regime (above 1,000 minutes) is about three times less.

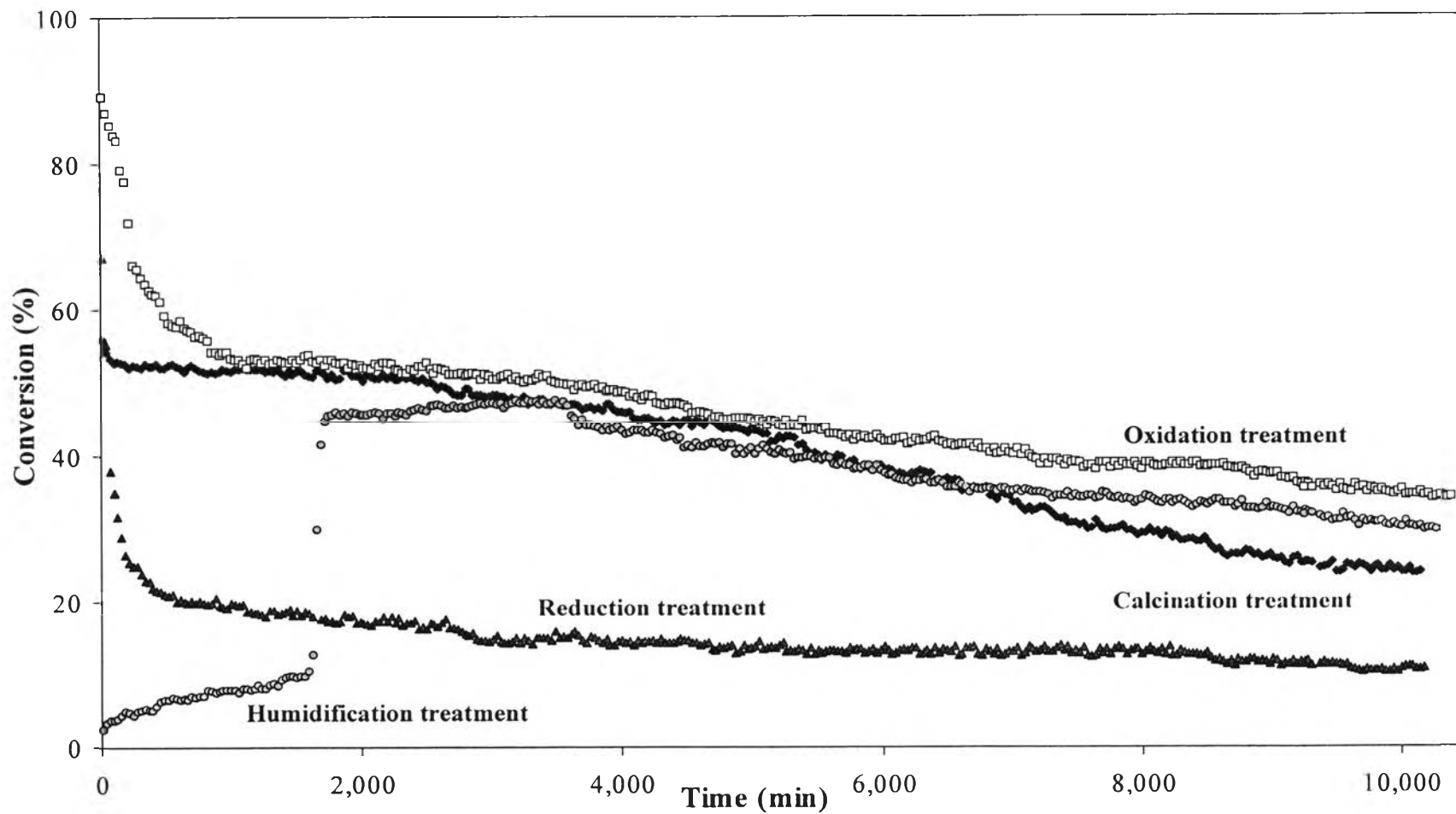


Figure 4.3 Deactivation Tests of 1% Silver Oxide Catalysts at 40 °C under Various Pretreatments.

Figure 4.4 illustrates the results of various sequential treatment strategies to regenerate the 0.1 percent silver catalyst after it was used for 10,000 minutes shown in Figure 4.1 to oxidize carbon monoxide. The first pretreatment was simple exposure to ambient air for one week. After this pretreatment the starting activity of the catalyst was not improved indicating that ambient air exposure does not deactivate or activate the catalysts. These catalysts were then stored in oxygen at room temperature for five days which resulted in a dead catalyst. It is not sure whether the observed result is real or it was due to some artifacts such as adsorbed water clogging the pores of the catalyst. Treatment of the dead catalyst in flowing oxygen for five days at 200 °C increased the initial activity of the catalyst to a high level, but the activity did not last long and a sharp activity decay lasting only about 200 minutes brought the activity of the catalyst down from 45 to 15 percent conversion. The initial decay period is followed by a period of gradual loss of activity slower activity after 2,000 minutes on stream as this catalyst was treated with humidified helium stream (saturated with water vapor at room temperature) at various temperatures and for various lengths of time. Exposure to humidified reactants at 30 °C resulted in an initial activity of almost zero conversion and increased slowly as the catalyst was losing the condensed water. Exposure to humidified reactants at 100 °C in contrast regenerated the activity of the catalyst to 30 percent conversion level. Treatment at 200 °C resulted in an even more active catalyst (36 percent initial conversion). However, extending the regeneration period to four days did not improve the activity further rather it resulted in a loss of activity all the ways down to 25 percent conversion. Reduction of this catalyst with hydrogen at 200 °C for 12 hours almost doubled the activity to 38 percent. Increasing hydrogen reduction period to four days at 200 °C provided some more gains in activity to 42 percent conversion. Finally leaving this catalyst in ambient air for one month resulted in total loss of activity.

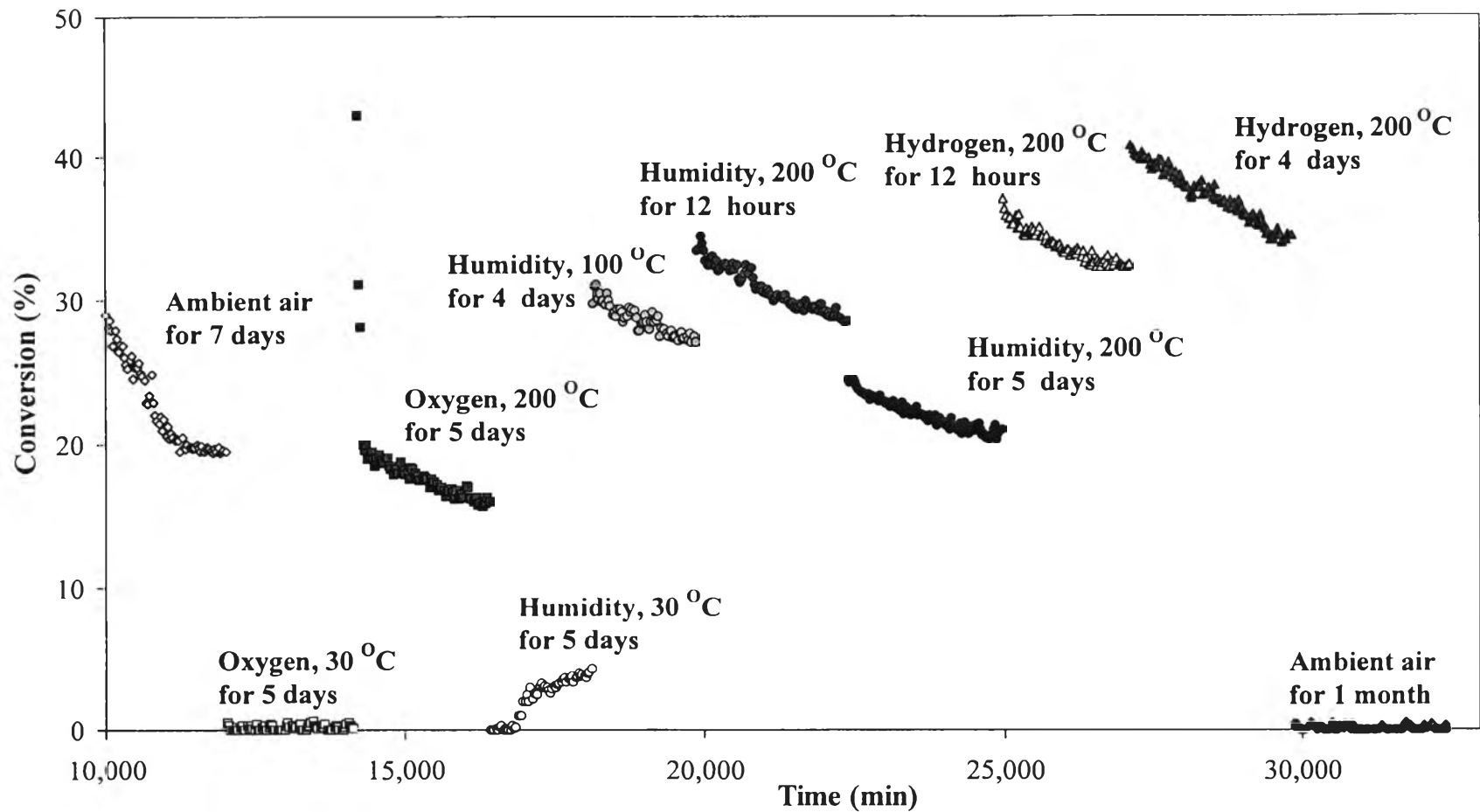


Figure 4.4 Regeneration Tests of 0.1% Deactivated Silver Oxide Catalysts at 50 °C.

Again it is believed that the activity loss is simply due to absorption of water vapor in the humid atmosphere of Bangkok and given enough time to evaporate all the water from the pores the catalyst would gain back its activity. It is important to note that none of the regeneration treatments increased the activity of this catalyst to more than half the initial activity of the fresh catalyst.

Figure 4.5 shows the conversion of carbon monoxide by two different catalysts loadings while keeping other factors constant. The amount of catalyst increases the conversion of carbon monoxide as expected. However, the increase is not linear with the amount of the catalyst and over the 10,000 minute test time the difference is only 10 percent more conversion between the 100 and 200 mg catalyst loadings.

Figure 4.6 illustrates a comparison of the activities of silver and gold catalysts with same metal loadings and same reducible metal oxides. This figure shows that even the activity of the gold containing catalysts is always higher, the difference is not very significant. The decay behaviors are also similar. These results imply that at low metal loadings the behavior of the catalyst is mainly determined by the support instead of by the metal, or alternatively only a very small amount of metal participates in the reaction.

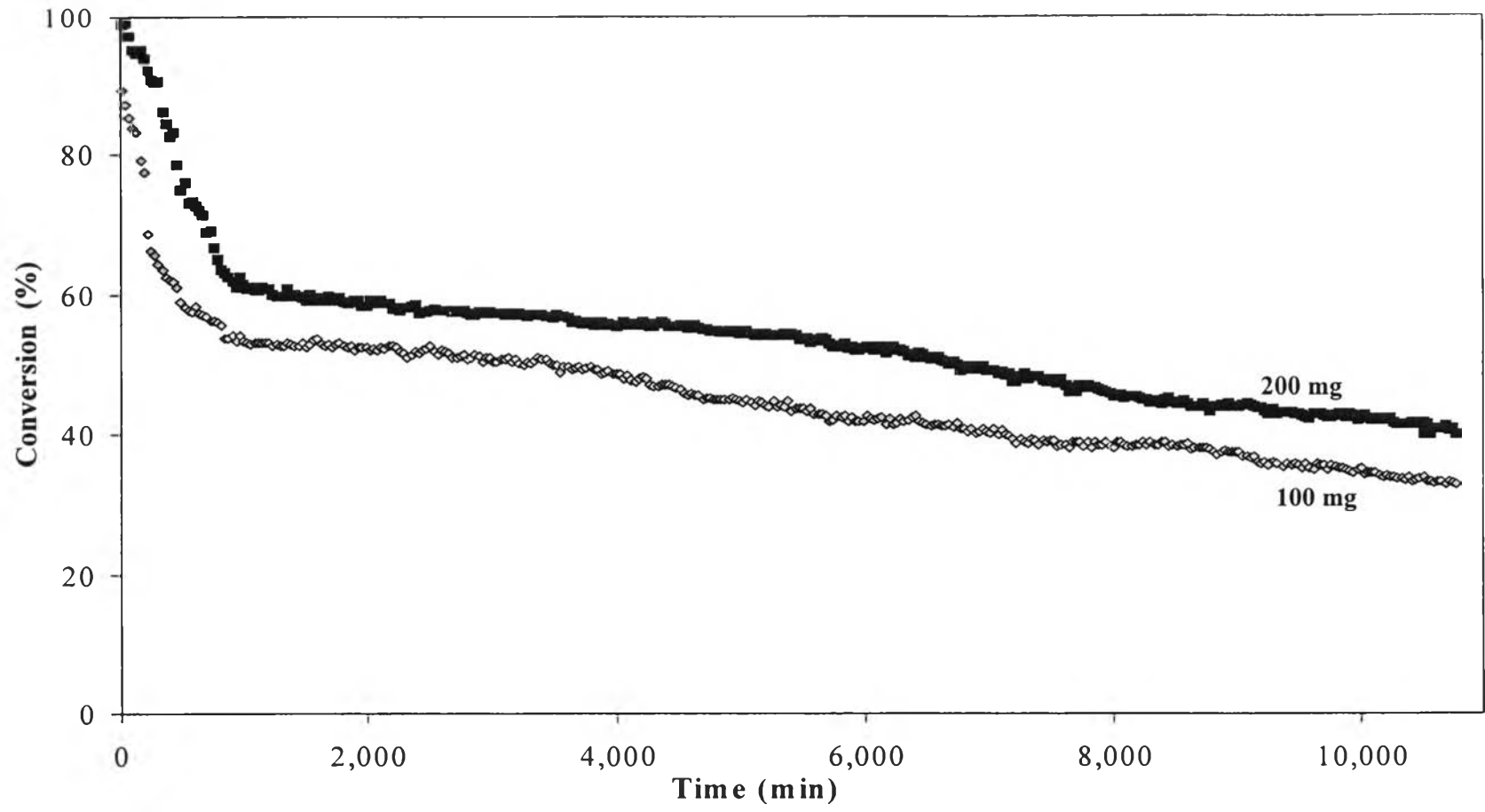


Figure 4.5 Deactivation Tests of 1%SilverOxides Catalysts at 40 °C after Oxygen Pretreatment.

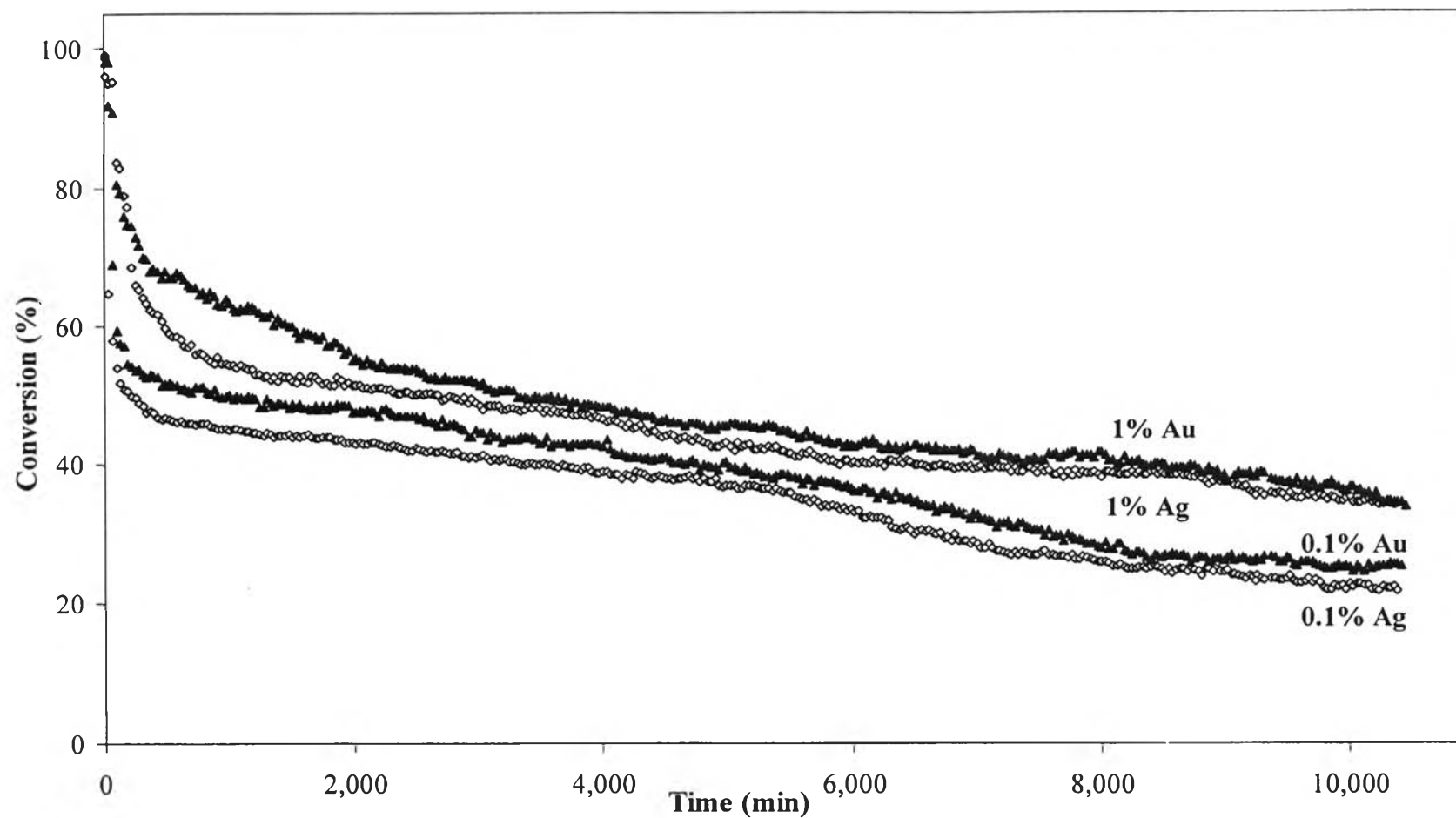


Figure 4.6 Deactivation Tests of Gold and Silver Oxide Catalysts at 40 °C after Oxygen Pretreatment.

4.2 Catalyst Characterization

In order to determine the molecular changes leading to the behaviors described above, a knowledge of the changes in catalyst itself is necessary. The BET surface area measurements, XRD, TEM and TG were used to measure the catalyst properties. before and after pretreatments to characterize and relate to the changes in catalytic activity observed. Table 4.2 gives BET surface areas of the silver catalysts used in this work as a function of calcination temperature. All catalysts containing higher than 20 percent of manganese have low surface areas. The surface areas of the high manganese containing catalysts increase after calcining at 300 °C, but they are still less than half of the surface areas of the high cobalt loading catalysts. Increasing the calcination temperature to 300 °C increases the surface areas of all catalysts. Also, as expected the surface area is independent of the amount of metal loading if other factors are the same.

Table 4.3 shows the phases of catalysts identified from the XRD analysis of all the fresh catalysts and one deactivated catalyst. This table shows that the precipitated manganese is in the form of a carbonate. The amount of crystalline MnCO_3 decreases and the amount of crystalline cobalt oxide (Co_3O_4) increases with increasing calcination temperature. The deactivated catalyst shows that the opposite has happened during the deactivation.

Table 4.4 shows that the oxidized catalyst at 200 °C has the highest surface areas. In contrast, the reduced and deactivated catalyst surface areas are rather the same. This decreased surface area may be due to the sintering of the support metal and increasing of inactive species.

Figures 4.7 and 4.8 illustrate the changes as a function of the calcination temperature and regeneration treatment. In Figure 4.7 it was seen that the manganese carbonate totally disappears after calcining at 300 °C. Also, the cobalt oxide crystallites increase dramatically both in amount and size in going from 100 to 300 °C. At 100 °C almost all of the cobalt oxide is in amorphous

form. Crystalline silver is present in a large crystallite form at 100 and 200 °C, but is not clearly detectable after calcining at 500 °C. Instead, the crystalline silver oxides will be formed. The silver oxide peak ($2\theta = 38.61$) is also difficult to detect because this peak shows on the shoulder of cobalt oxides.

Figure 4.8 shows that a deactivated catalyst has manganese carbonate in large amounts which is reduced by hydrogen reduction and oxidation. However, hydrogen reduction also reduces the amount of cobalt oxide (Co_3O_4) and increases the crystallite size of the silver. Oxidation also appears to reduce the amount of manganese carbonate and the metallic silver without decreasing the amount of cobalt oxide.

Figure 4.9 shows a high resolution TEM micrograph of one percent silver catalyst calcined in air at 200 °C. It can be found that small silver particles are uniformly dispersed on the reducible metal oxides of sizes around 5-10 nm and Figure 4.10 illustrates the micrograph of the same catalyst after passing through reactant gases 10,000 minutes on stream which the metal supports is sintered as silver metal still dispersed.

Figure 4.11 shows the thermogravimetric analysis results for the 0.1 percent silver containing catalysts. The catalysts dried at 100 °C exhibit several distinct transformations. There is continuous weight loss until 200 °C at which point the decrease in weight accelerates and illustrates a distinct step at about 270 °C. The continuous weight decreases as well as the changing in step is found due to the decomposition of the manganese carbonate. The second large step change observed at 350 °C is due to the decomposition of Co_3O_4 to CoO . The catalyst calcined at 200 °C has only one change in step centered around 300 °C which interpreted as the simultaneous decomposition of cobalt oxide and manganese carbonate. The catalyst calcined at 300 °C does not show any of the step changes in weight loss due to decomposition. All of the catalysts have a slight weight loss around 100 °C which is attributed to loss of adsorbed moisture.

Table 4.2 BET Surface Area Measurement (m^2/g) of Silver Oxide Catalysts

Catalysts	Catalysts dried at $100\text{ }^\circ\text{C}$	Catalysts calcined at $200\text{ }^\circ\text{C}$	Catalyst calcined at $300\text{ }^\circ\text{C}$
0.1%Ag99.9%Co	114.7	128	133
0.1%Ag99.9%Mn	17.16	15.96	28.27
0.1%Ag89.9%Co10%Mn	135	127.2	148.70
0.1%Ag69.9%Co30%Mn	53.65	48.99	131.2
0.1%Ag49.95%Co49.95%Mn	21.22	18.12	52.64
0.1%Ag30%Co69.9%Mn	20.96	17.88	36.04
0.1%Ag10%Co89.9%Mn	18.18	16.80	33.70
0.1%Ag80%Co19.9%Mn	72.72	87.84	139.12
1%Ag79.3%Co19.7%Mn	80.50	91.96	141.19
5%Ag76.1%Co18.9%Mn	79.91	65.97	125.66

Table 4.3 Phase Identification of the Silver Oxide Catalysts

Catalysts	Catalysts dried at 100 °C	Catalysts calcined at 200 °C	Catalysts calcined at 300 °C
0.1%Ag99.9%Co	CoO Co ₃ O ₄	↓CoO Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
0.1%Ag99.9%Mn	MnCO ₃	↓MnCO ₃	-
0.1%Ag89.9%Co10%Mn	MnCO ₃ CoO, Co ₃ O ₄	↓MnCO ₃ ↓CoO, Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
0.1%Ag69.9%Co30%Mn	MnCO ₃ CoO, Co ₃ O ₄	↓MnCO ₃ ↓CoO, Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
0.1%Ag49.95%Co49.95%Mn	MnCO ₃ CoO, Co ₃ O ₄	↓MnCO ₃ ↓CoO, Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
0.1%Ag30%Co69.9%Mn	MnCO ₃ CoO	↓MnCO ₃ ↓CoO, Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
0.1%Ag10%Co89.9%Mn	MnCO ₃	↓MnCO ₃ Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
0.1%Ag80%Co19.9%Mn	MnCO ₃ CoO, Co ₃ O ₄	↓MnCO ₃ ↓CoO, Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
1%Ag79.3%Co19.7%Mn	MnCO ₃ CoO, Co ₃ O ₄	↓MnCO ₃ ↓CoO, Co ₃ O ₄ ↑	Co ₃ O ₄ ↑
5%Ag76.1%Co18.9%Mn	Ag, MnCO ₃ CoO, Co ₃ O ₄	↓Ag, MnCO ₃ ↓ ↓CoO, Co ₃ O ₄ ↑	↓Ag Co ₃ O ₄ ↑
5% Deactivated Silver Catalysts after 10,000 minutes	-	↑Ag, MnCO ₃ ↑ ↓Co ₃ O ₄ , CoO↑	-

Note : The results at 200 and 300 °C are compared with 100 °C.

Table 4.4 Comparison of the Surface Area of 0.1% Silver Oxide Catalysts

Catalyst environment	Surface area (m ² /g)
Calcined catalysts at 200 °C for 4 hours	87.84
Oxidized catalysts at 200 °C for 4 hours	100.05
Reduced catalysts at 200 °C for 4 hours	84.10
Deactivated catalysts at 40 °C for 1 week	84.37

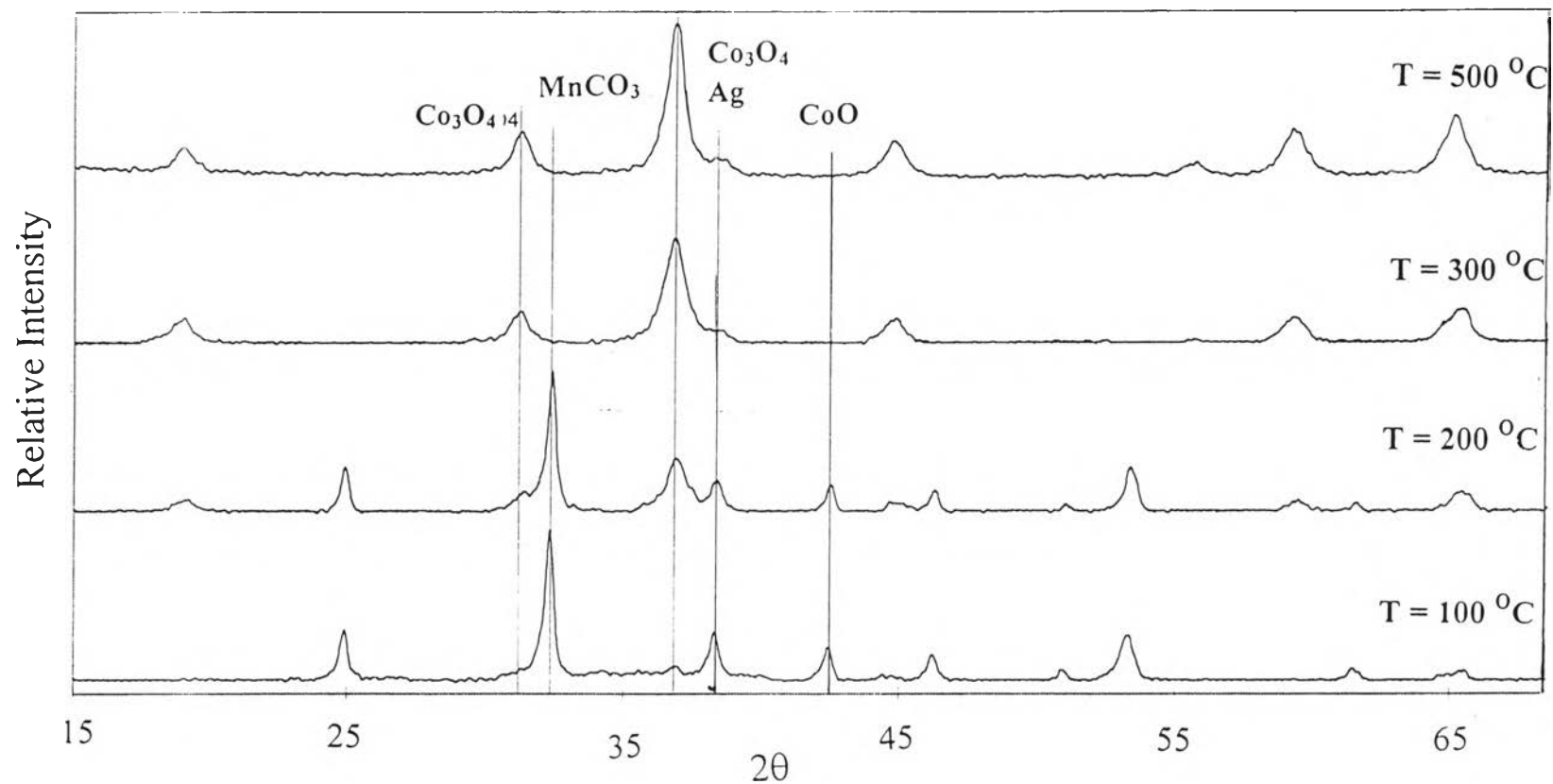


Figure 4.7 X-ray Spectra of 5% Silver Oxide Catalysts.

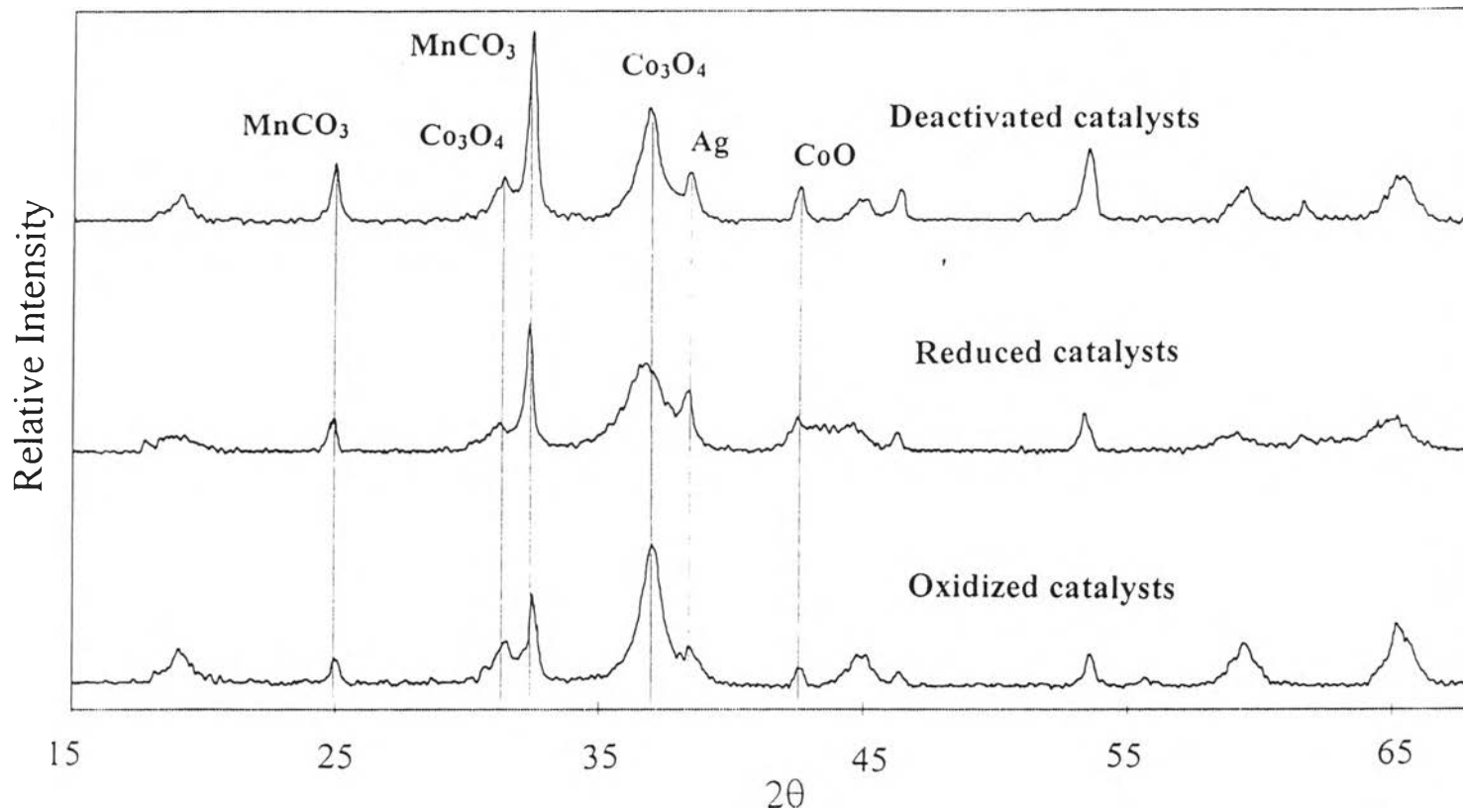


Figure 4.8 X-ray Spectra of 5% Silver Oxide Catalysts Calcined at 200 °C under Different Environment.

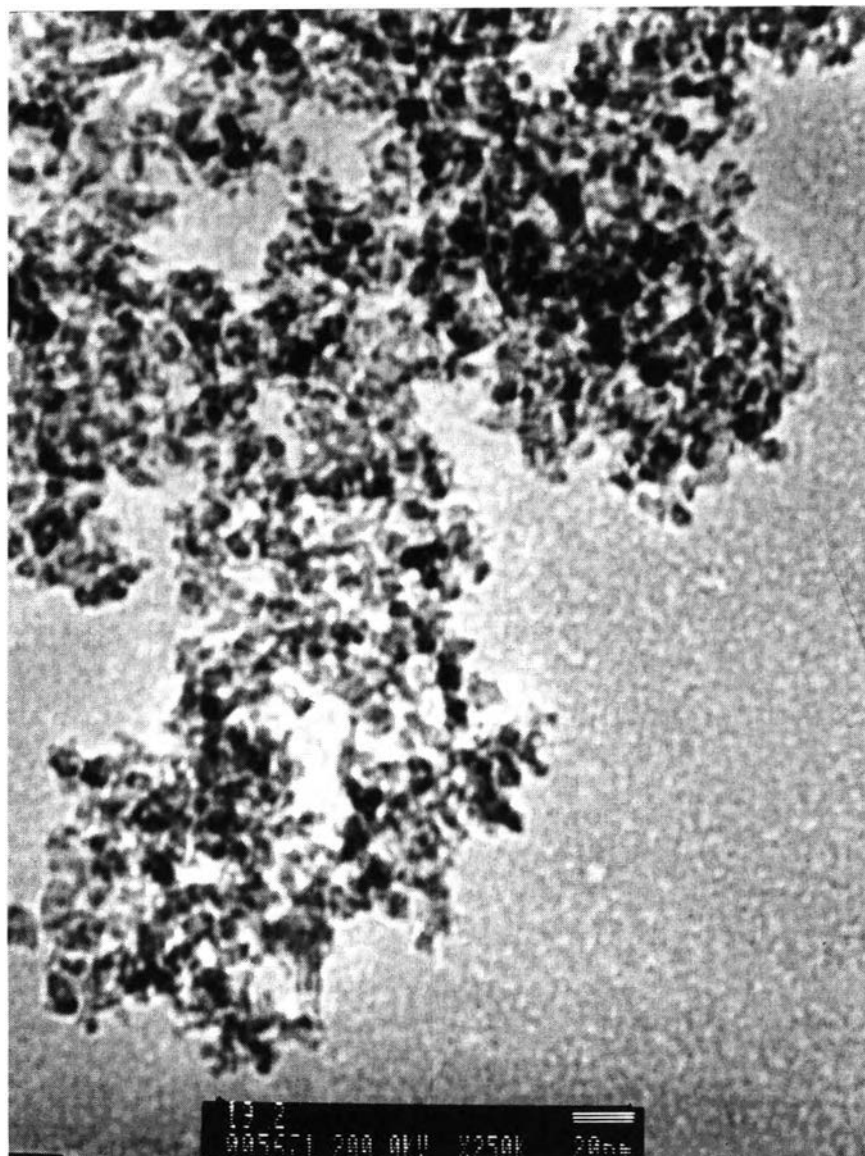


Figure 4.9 TEM Micrograph of 1% Silver Oxide Catalysts
Calcined at 200 °C (Magnification :x250K).

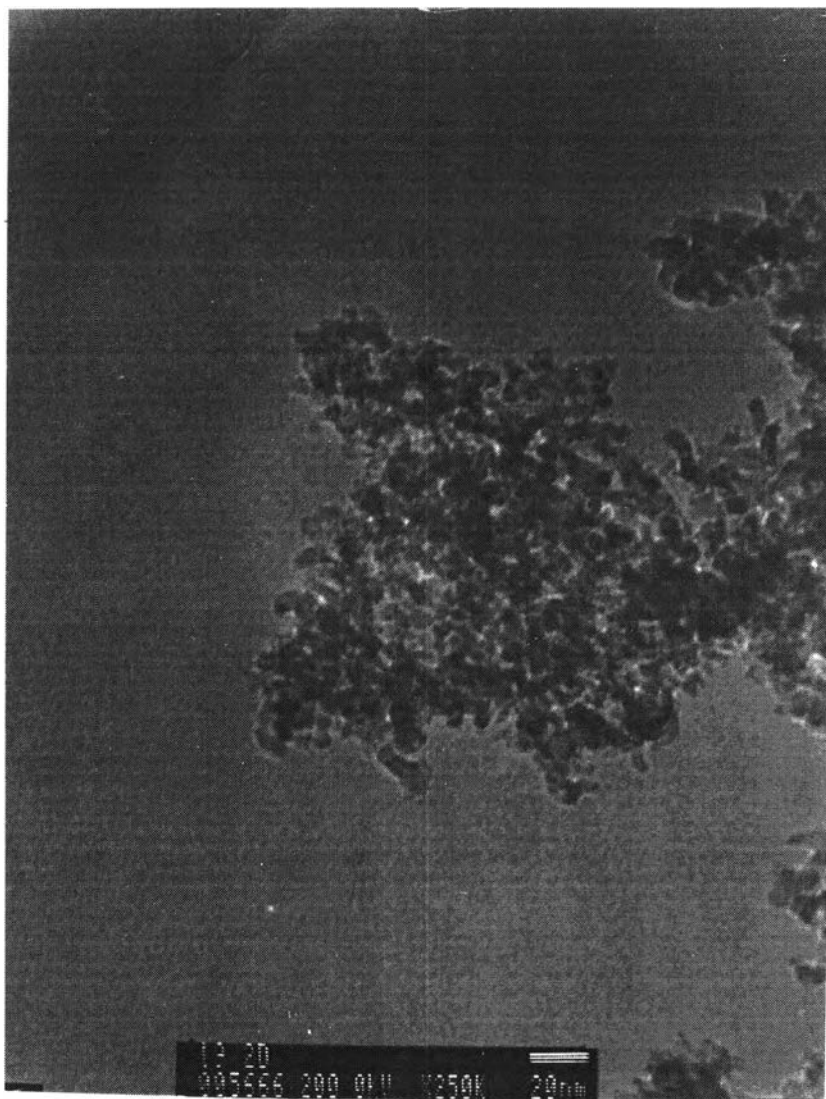


Figure 4.10 TEM Micrograph of 1% Deactivated Silver Oxide Catalysts Calcined at 200 °C (Magnification:x250K).

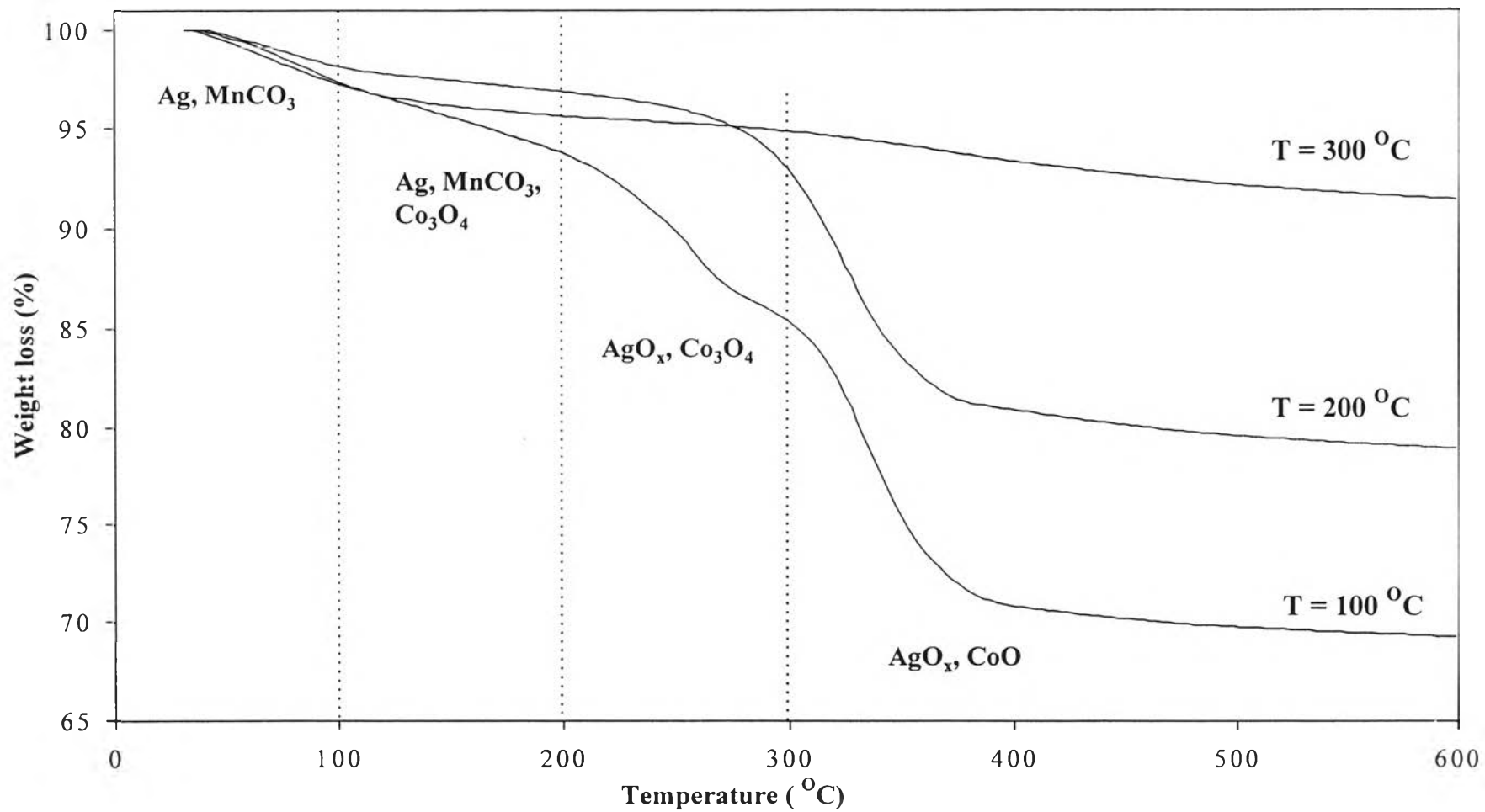


Figure 4.11 Thermogram of 0.1% Silver Oxide Catalysts under Nitrogen Environment.

Table 4.5 is a comparison of these results with others. These composite silver oxide catalysts are very active, in agreement with the previous findings. However, there are also significant differences in the behavior of these catalysts with respect to hydrogen reduction and various pretreatments. Unlike the results of Srivannavit, S. and Sze, C., it was found that hydrogen reduced catalysts are still active even though the activity is only 30 percent of the activity of an oxidized fresh catalysts.

Table 4.5 Comparison of Oxidation Activities of Various CO Oxidation Catalysts at 50 °C

Catalysts	Experimental conditions	Rate micro mol/g/min	Reference
Ag/MnO_x/Co₃O₄ 0.1% Ag	0.01% CO, 20% O₂ SV = 30,000 ml/g.hr	8.54	This work (1997)
Ag/MnO _x 50% Ag	1% CO, 20% O ₂ SV = 120,000 ml/g.hr	500	Srivannavit, S. (1996)
Ag/MnO _x 1% Ag	1% CO, 0.5% O ₂ SV = 4,000 ml/g.hr	14	Gardner et al. (1991)
Au/Fe ₂ O ₃ 5% Au	1% CO, 20% O ₂ SV = 200,000 ml/g.hr	2000	Sze, C. (1995)
Au/Fe ₂ O ₃ 5% Au	1% CO, 0.5% O ₂ SV = 4,000 ml/g.hr	6.5	Gardner et al. (1991)
Au/Fe ₂ O ₃ 5% Au	1% CO, 20% O ₂ SV = 10,000 ml/g.hr	199	Haruta et al. (1989)
Au/MnO _x 10% Au	1% CO, 0.5% O ₂ SV = 20,000 ml/g.hr	1.2	Gardner et al. (1991)
Pt/SnO _x 19.5% Pt	1% CO, 0.5% O ₂ SV = 4,000 ml/g.hr	30	Gardner et al. (1991)