

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Temperature of 50% Conversion ($T_{1/2}$) Test

Figures 4.1 and 4.2 show the relationship between temperature and %CO conversion of silver and gold on different supports, respectively. $T_{1/2}$, the temperature giving 50% CO conversion for all the catalysts, was found from the two figures and is tabulated in table 4.1. Lower $T_{1/2}$ indicated relatively greater catalytic activity (Haruta and Sano, 1983). From the $T_{1/2}$ results tabulated in Table 4.1, Mn-Co support was observed to be the most active support of both silver and gold catalyst. Furthermore, the pretreatment effect on the catalytic activity was tested. It was found that pretreated catalysts had greater activity than non-pretreated catalysts. Not only the nature of supporting oxide was important but the pretreatment procedure could also have an impact on the catalyst activity (Tanielyan and Augustine, 1992).

In Figure 4.1, pretreated silver catalysts were observed to have higher activity at the beginning. After that the activity dropped dramatically and then increased back again at higher temperature. This result could be explained by oxygen chemisorption. Oxidation pretreatment caused the silver catalyst surface to be oxygen rich. Both fresh oxygen surface and gas phase oxygen from the reactant gas were utilized (Gardner et al., 1991) leading to higher activity initially. Oxygen chemisorption was not observed in gold catalysts owing to the difficulty of gold to form surface oxide.

Surface area and average pore size of catalysts were given in Tables 4.2 and 4.3, respectively. Based on the fact that the higher surface area catalyst

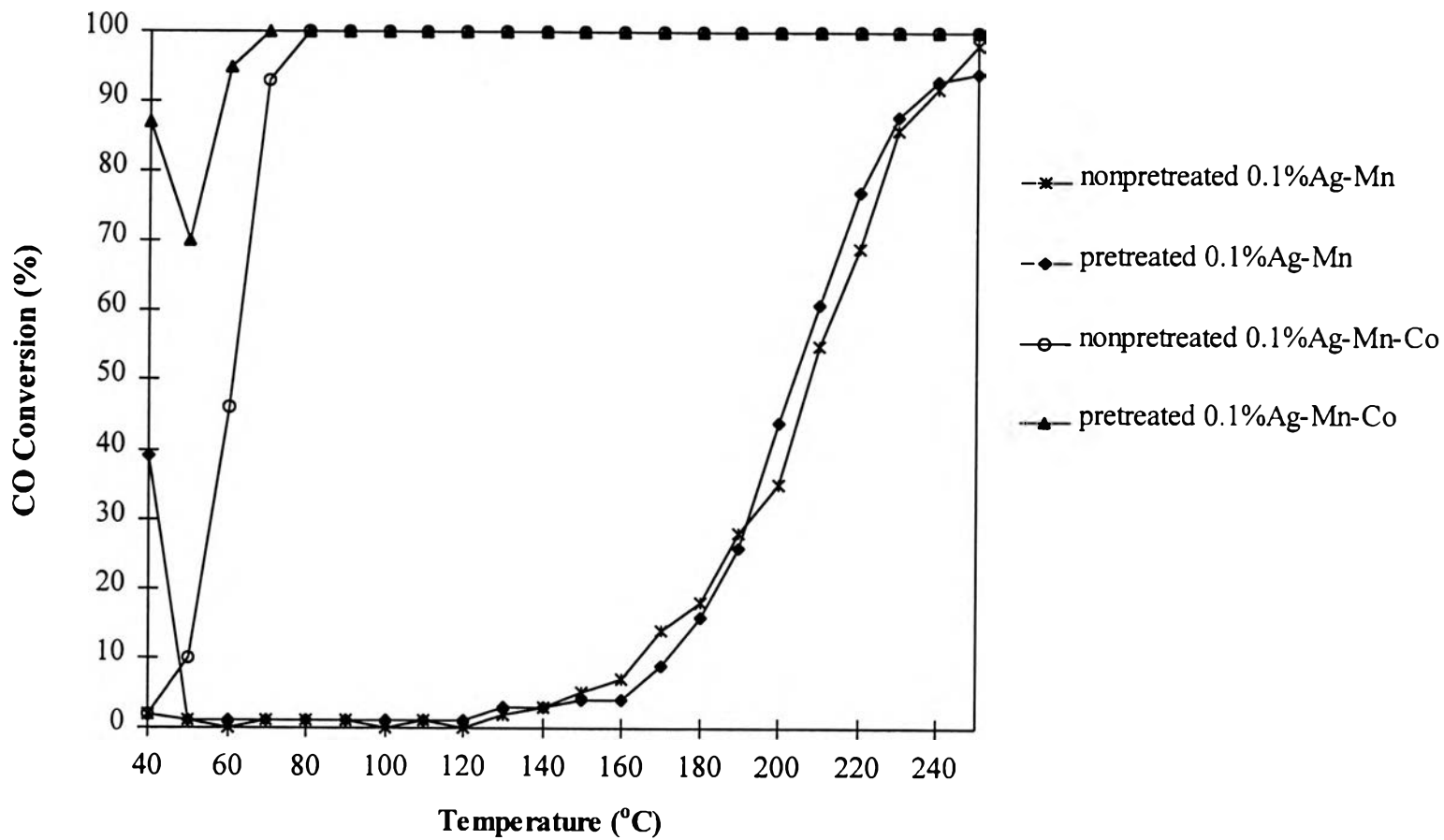


Figure 4.1 Temperature and CO conversion of silver catalysts.

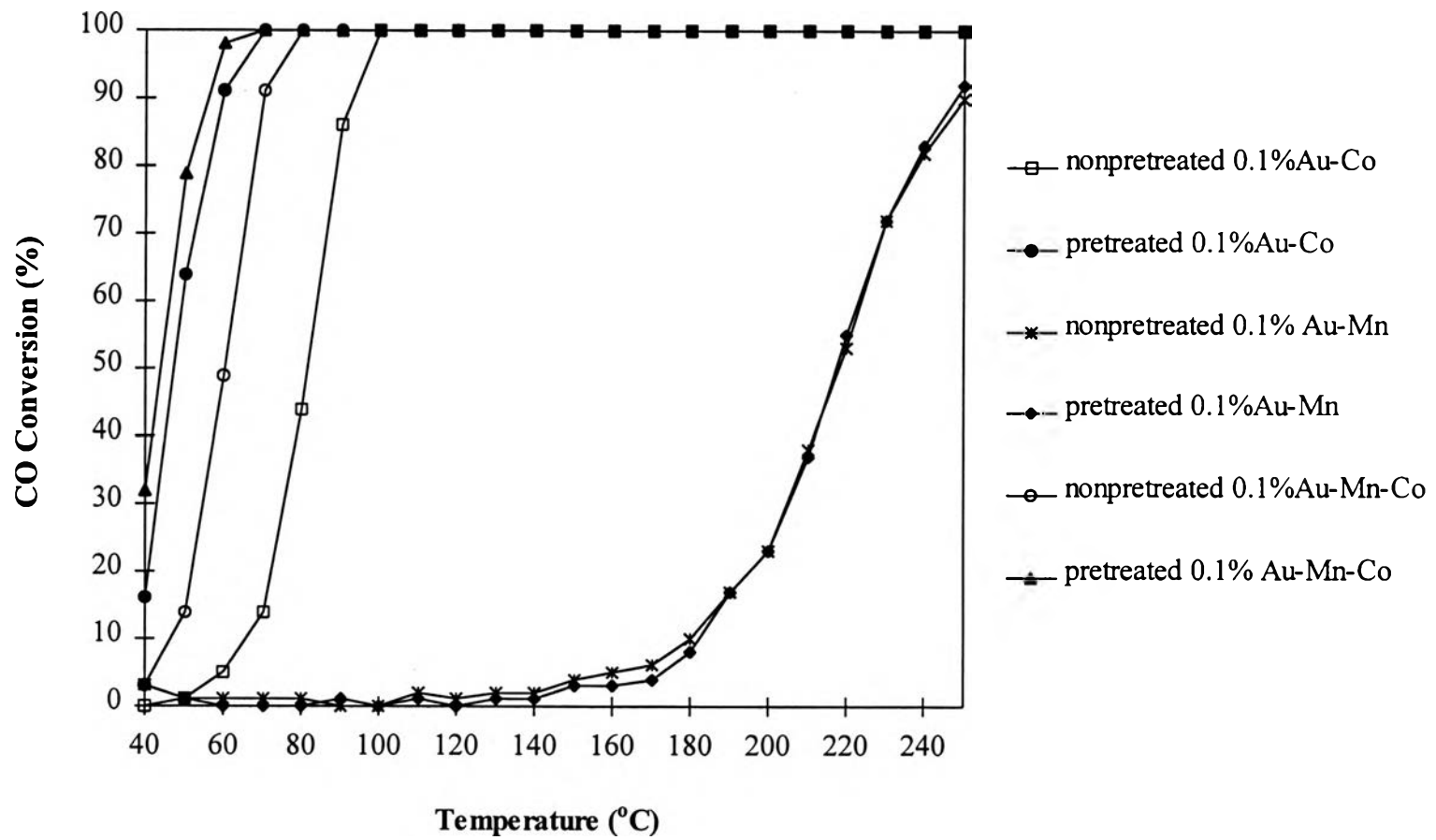


Figure 4.2 Temperature and CO conversion of gold catalysts.

Table 4.1 Temperature for 50% conversion

Catalyst	T _{1/2} (°C)	
	Non-pretreated	Oxidation pretreated
0.1%Ag-Mn	207	204
0.1%Ag-Mn-Co	61	*
0.1%Au-Co	82	47
0.1%Au-Mn	218	217
0.1%Au-Mn-Co	60	44

Note : * = The conversion was greater than 50%.

Table 4.2 BET surface area (m²/g) of catalysts

Catalyst	Surface area (m ² /g)	
	Non-pretreated	Oxidation pretreated
0.1%Ag-Mn	7.99	7.13
0.1%Ag-Mn-Co	157.80	142.00
0.1%Au-Co	202.70	181.00
0.1%Au-Mn	9.27	5.14
0.1%Au-Mn-Co	190.10	148.70

Table 4.3 Average pore radius of catalysts

Catalyst	Pore radius (°A)	
	Non-pretreated	Oxidation pretreated
0.1%Ag-Mn	4.57	6.93
0.1%Ag-Mn-Co	6.88	7.30
0.1%Au-Co	7.60	7.61
0.1%Au-Mn	5.91	7.44
0.1%Au-Mn-Co	6.87	7.02

tended to be more active. Mn supported catalyst had lower surface area than Mn-Co and Co supported catalysts, respectively. Even though Co supported catalyst had the highest surface area, it had lower activity than Mn-Co supported catalyst due to synergistic effect between Mn and Co. All Pretreated catalysts had lower surface area than non-pretreated catalysts. However, they had higher activity. Since they were activated by pretreatment procedure (Tanielyan and Augustine, 1992).

4.2 Deactivation Test

Based on the $T_{1/2}$ results, the Mn-Co supported catalyst was identified to be the most active catalyst. Both silver and gold on Mn-Co support catalysts were further investigated for the long term activity and stability. The effect of the amount of silver and gold catalyst observed at 60°C is illustrated in Figures 4.3 and 4.4, respectively. The activity of the 0.1g silver catalyst fast decayed

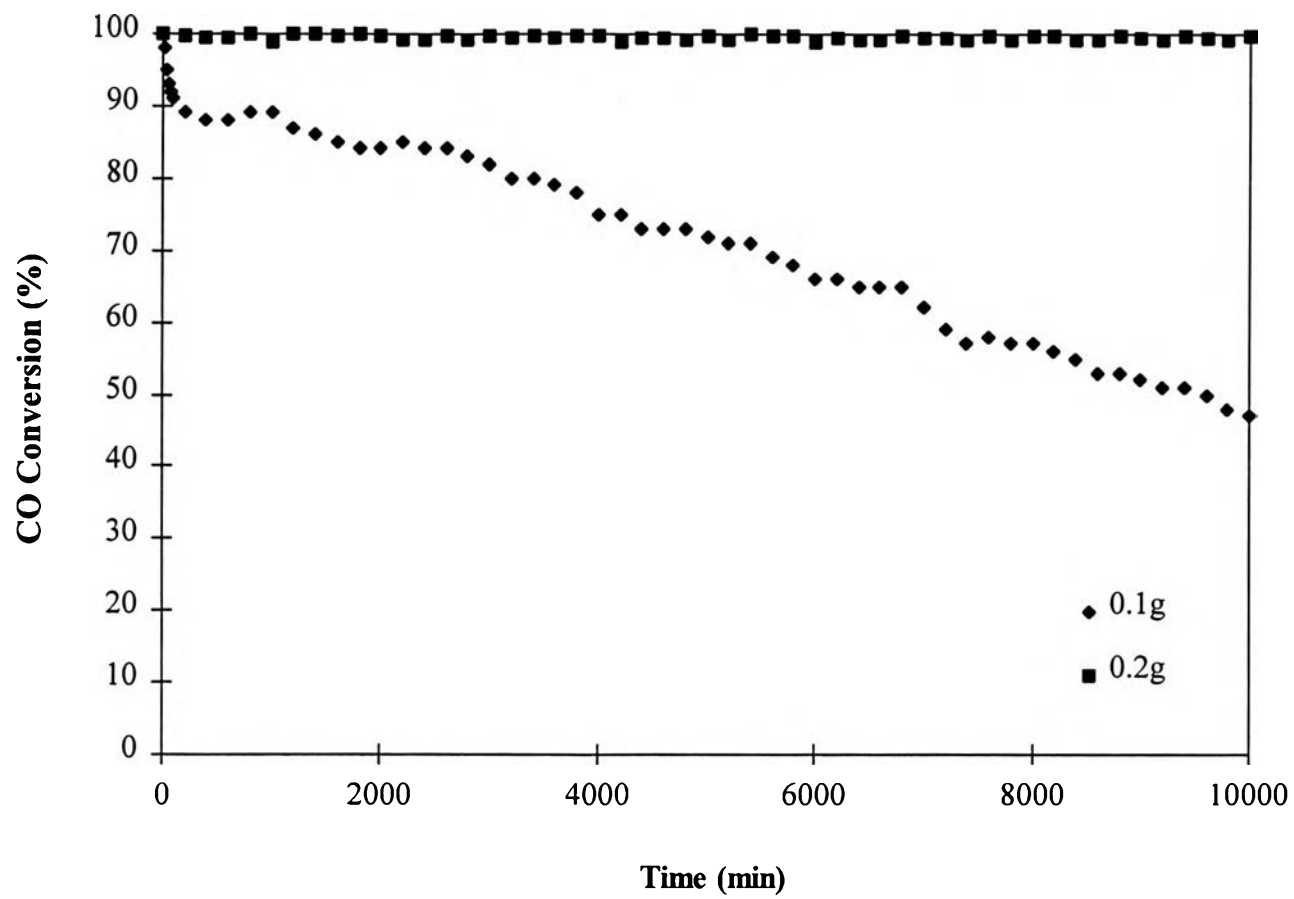


Figure 4.3 Deactivation test of 0.1%Ag-Mn-Co at 60°C.

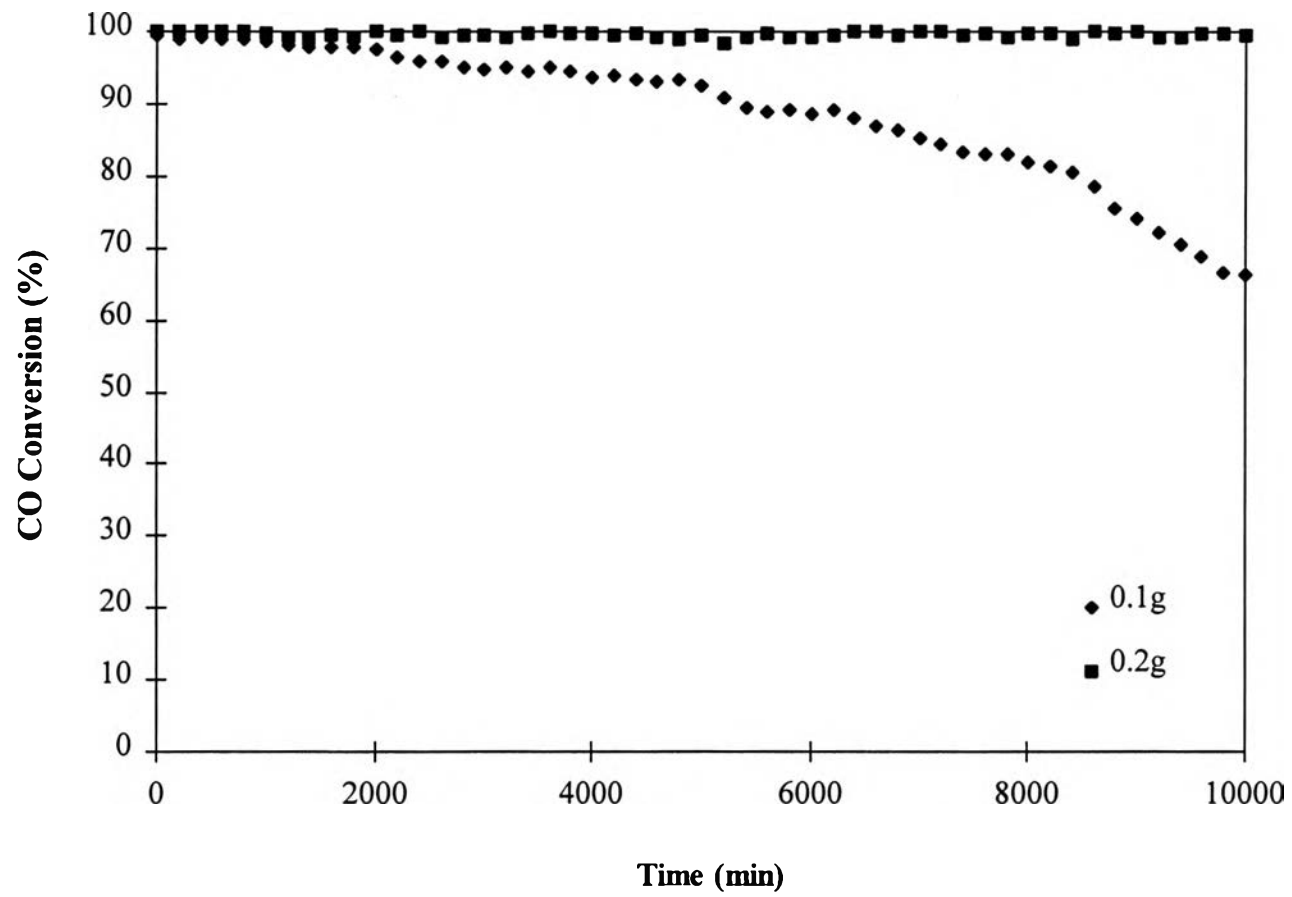


Figure 4.4 Deactivation test of 0.1%Au-Mn-Co at 60°C.

from 100% CO conversion during the first 100 minutes and slowly decayed after that. On the other hand, no fast decay region was observed with the gold catalyst. Gold catalyst had 100% CO conversion initially and followed by a slow decay. This showed that intrinsic activity of gold catalyst was 100% CO conversion at 60°C while that of silver catalyst was about 90% CO conversion. The final catalyst activity at 10,000 min of silver was about 50% CO conversion whereas gold was about 65% CO conversion. Therefore, gold catalyst was more active than silver catalyst.

For both silver and gold catalysts, when the amount of catalyst was increased to 0.2g, conversion of CO increased to 100% and stayed at this level throughout the 10,000 min. Time on stream of 0.3g silver catalyst, shown in Figure 4.5, was extended to 30,000 min. It still maintained 100% conversion with negligible decay throughout this long period. Not only high activity was observed but it also showed the stability over long period.

The effect of the temperature on the activity is illustrated in Figure 4.6. The temperature was decreased to 50 and 40°C, respectively after 10,000 min. Both silver and gold catalysts would maintain 100% CO conversion at 60°C. At 50°C, silver catalyst was 85% conversion whereas for the gold catalyst it was about 90%. At 40°C, both catalytic activities dropped to the same level to about 35% conversion.

From Figure 4.6 we can obtain an estimate of the activation energy. If we assume first order dependence on CO, using an integral reactor model, we obtain $E_a \sim 30$ kcal/gmole-K. If we assume a differential reactor model, we get ~ 14 kcal/gmole-K. These are on both sides of typical CO oxidation activation energy of ~ 22 kcal/gmole-K observed for Pt group metals.

Gold catalyst was further investigated by increasing the temperature back to 50 and 60°C, respectively. Based on the fact that physically adsorbed gas should easily desorb at higher temperatures, this test was conducted to

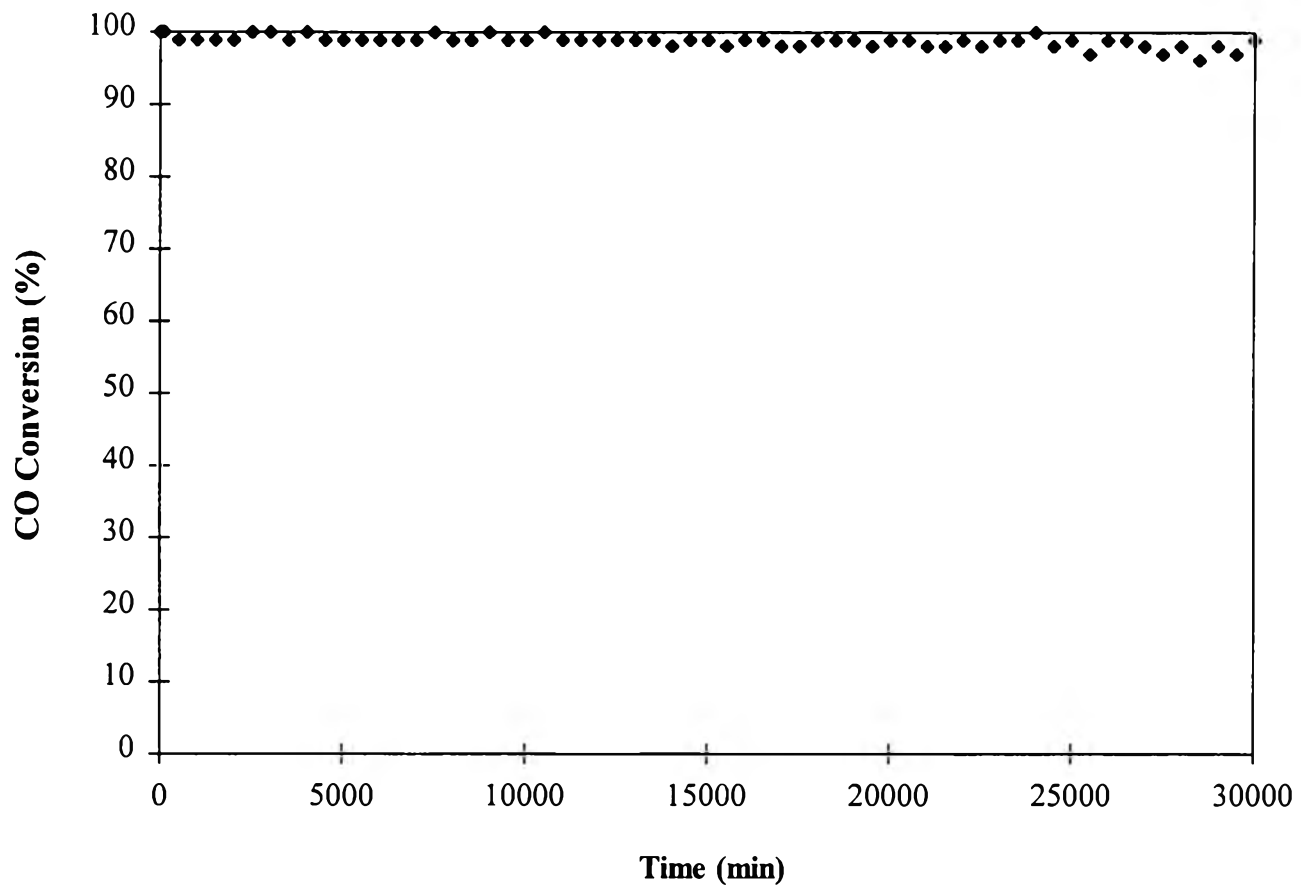


Figure 4.5 Deactivation test of 0.3 g 0.1%Ag-Mn-Co at 60°C.

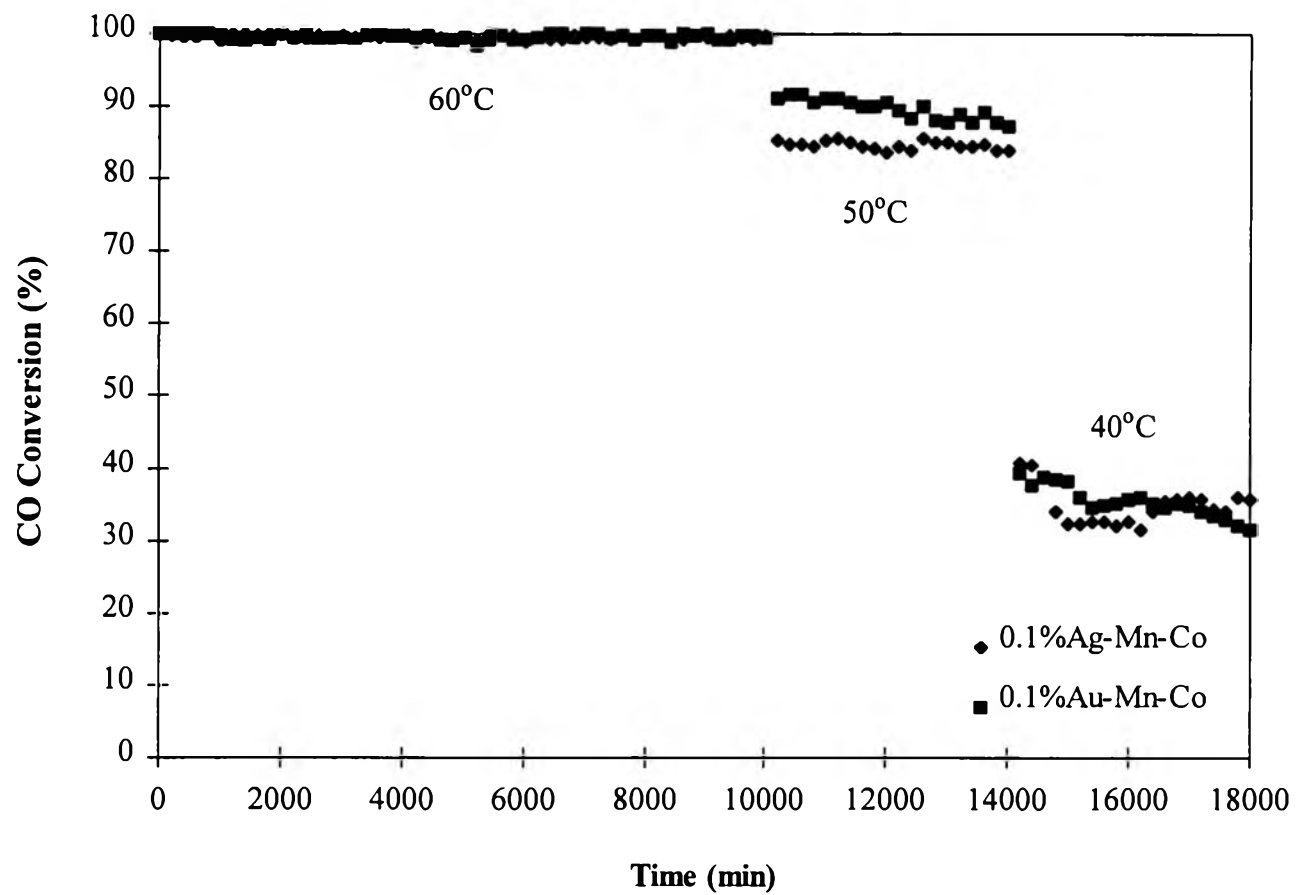


Figure 4.6 Deactivation test of 0.2 g catalyst at different temperatures.

observe the effect of carbonaceous species accumulated on the catalyst at low temperatures on the catalytic activity. The catalyst behavior is shown in Figure 4.7. The activity immediately increased back to 77% conversion, about 10% less than previous activity at 50°C. The activity also increased back to about 100% conversion with further increase of temperature to 60°C. At low temperature, apparently the CO remaining on the surface existed either as a non-reactive species or CO₂ produced did not desorb but stayed on the catalyst surface in a CO₂ or CO₃²⁻ state (Tanielyan and Augustine, 1992). These surface species contributed to the decay of catalytic activity as they decreased the surface availability for surface reaction with oxygen. Based on the result of the experiment with gold, the carbonaceous species formation is not a serious problem in this work. So low temperature operation did not seriously cause irreversible decay.

The above results indicated that these catalysts had high activity. So we were interested in determining from which part of the catalyst the catalytic activity came. The activity of gold and silver catalyst at 50°C was investigated and compared to the activity of the Mn-Co support. The result is shown in Figure 4.8. Gold performed better than silver and Mn-Co support, respectively. However, the difference between the gold and silver containing catalysts and the support is not large indicating that the support itself is responsible for majority of the activity.

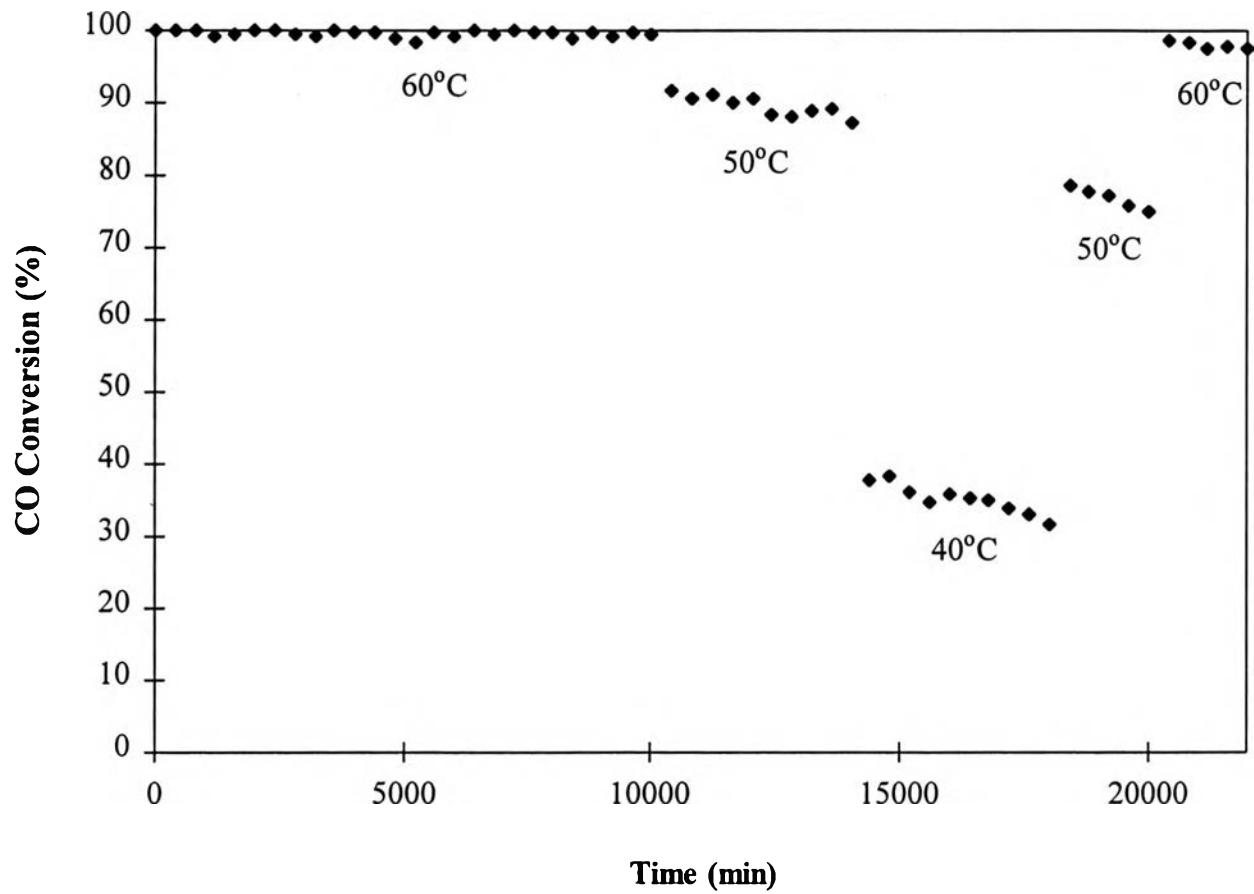


Figure 4.7 Deactivation test of 0.2 g 0.1% Au-Mn-Co at different temperatures.

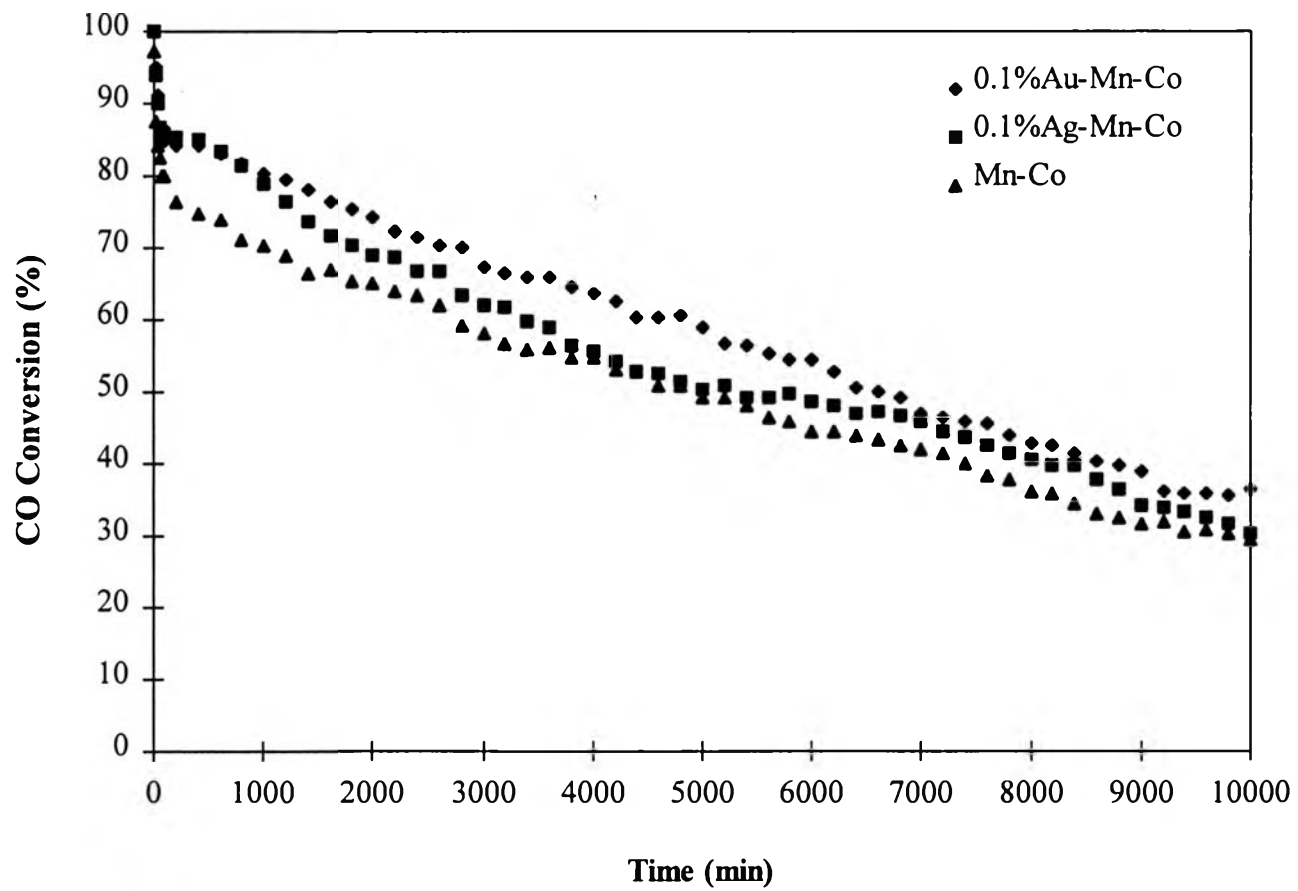


Figure 4.8 Deactivation test of 0.1 g catalyst at 50°C.

4.3 Regeneration Test

The catalyst deactivation was observed during the reaction possibly due to carbonate formation on the support. We did several experiments to see if the catalyst could be regenerated. Because of slow catalyst decay, the deactivation was accelerated by introducing carbon dioxide to the reactant gas mixture. When exposed to 3.22% CO₂, both silver and gold catalysts were deactivated to about 15% conversion. The activity recovery of gold and silver catalysts by various oxidation regeneration conditions are shown in Figures 4.9 and 4.10, respectively. Gold recovery activity was first considered. The activity of the catalyst oxygen regenerated at 110°C and 200°C were initially low but rapidly increased during first ~ 100 minutes after which a slow decay as seen with the fresh catalysts was observed. The initial low activity is probably due to residual CO₂ left on the catalyst which did not desorb.

The other two regenerations, two days of 200°C and 12 hrs 300°C led to catalysts with chemisorbed oxygen which was responsible for the high initial activities. However after ~ 100 minutes, the activity decay slowed down after the surface oxygen was exhausted.

The carbon dioxide desorption observed in the reactor effluent during regeneration period confirmed that the oxygen regeneration could expel carbonaceous species from the surface leading to activity restoration. A surprising result seen in Figure 4.9 was that the regeneration treatment at 200 °C resulted in lower activity recovery compared to 110 °C regeneration. This was most likely due to combined effects of accelerated sintering and desorption seen at the higher temperature.

When the regeneration time at 200°C was extended from 12 hr to 2 days. The activity was very high at the beginning compared to 12 hr regeneration. The longer regeneration period leading to more completely removal of

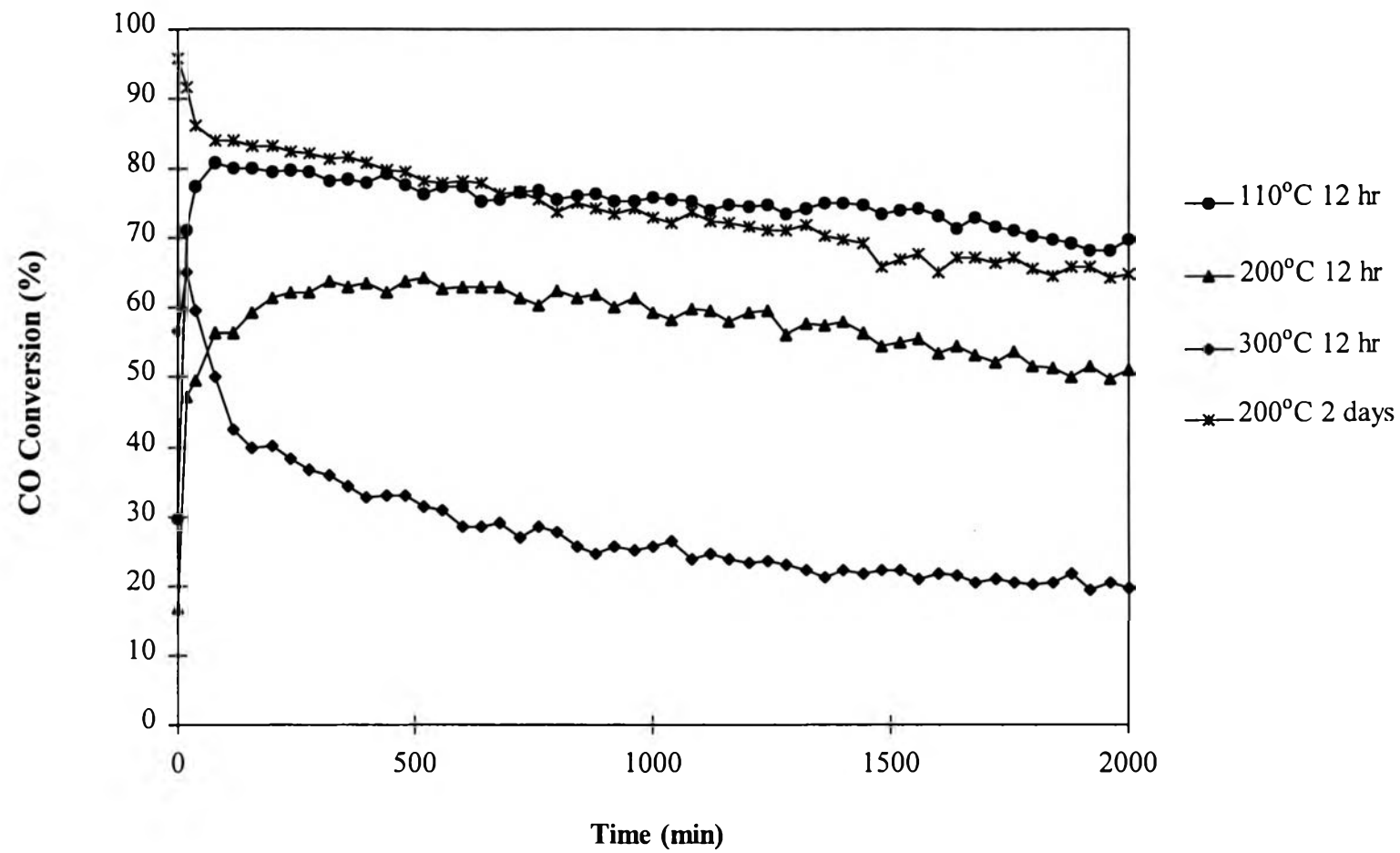


Figure 4.9 Oxidation regeneration test of 0.1%Au-Mn-Co at 50°C.

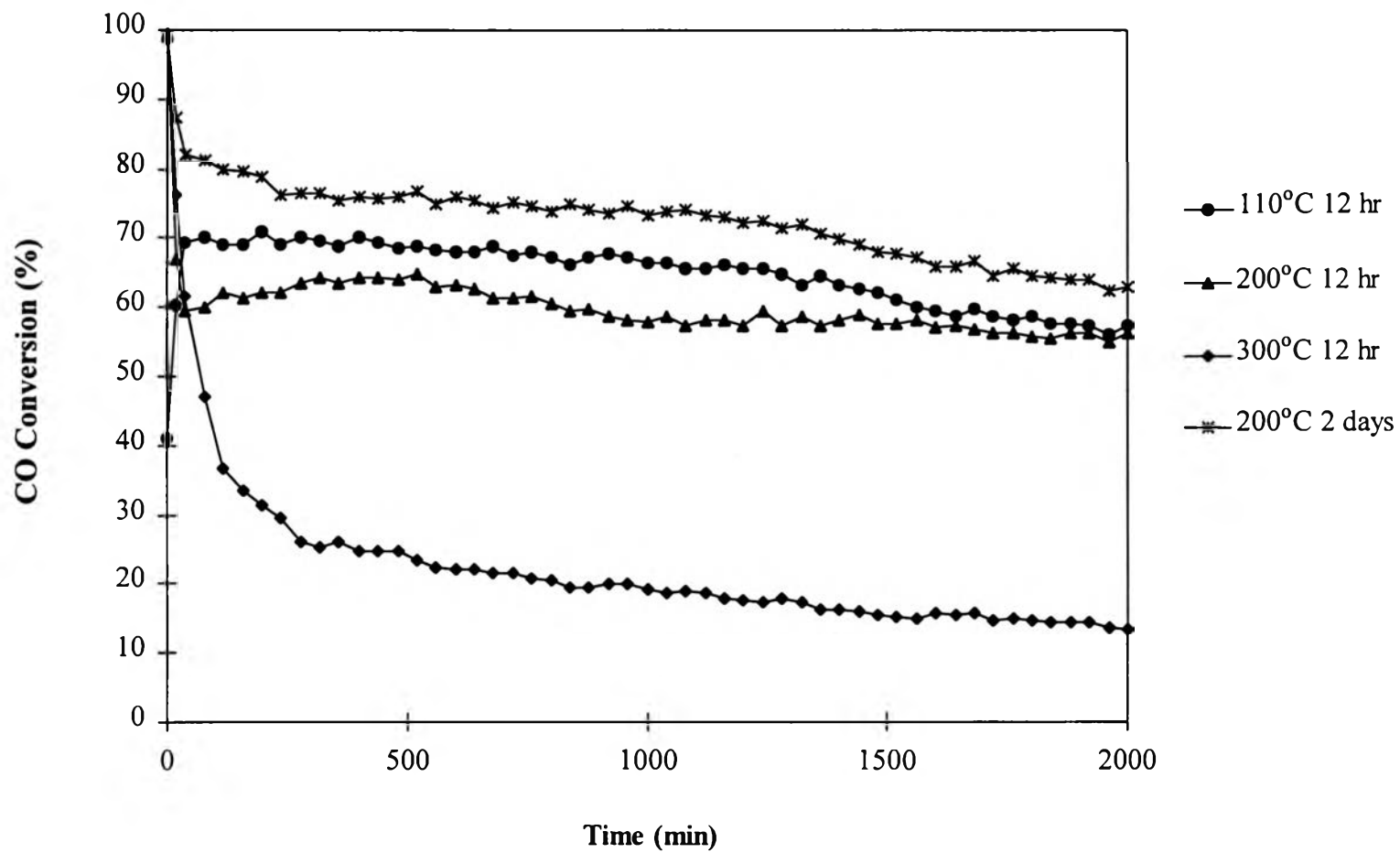


Figure 4.10 Oxidation regeneration test of 0.1%Ag-Mn-Co at 50°C.

carbonaceous deposit.

The silver catalyst oxidation regeneration treatment results shown in Figure 4.10 were similar to the gold catalyst results. Silver catalysts also lost activity when regenerated at 200°C but less than that of gold catalyst. Thus, silver catalyst tended to be more thermally stable than the gold catalyst.

The results of the oxidation regeneration experiments showed that longer oxygen treatments at lower temperatures were preferable to shorter treatments at higher temperatures. Higher temperatures led to faster decay of catalyst activity.

Another method to regenerate the catalyst employed in this study was by hydrogen reduction. Figures 4.11 and 4.12 describe the revived activity of silver and gold catalyst respectively. Reduction regeneration at 200°C of silver catalyst yielded higher activity than that at 110°C regeneration. This result was based on the fact that higher temperature regeneration was more effective to eliminate the contaminant on the catalyst surface. On the other hand, the higher temperature did not have any affect for the gold catalyst. The activity after 110°C and 200°C regeneration was about the same. The reduction temperature of 110°C was effective enough to activate the catalyst.

Overall for gold oxidation regeneration was better, for silver reduction regeneration was better leading to ~ 10% higher activity.

We speculate that during reduction regeneration the surface CO₂ was replaced by surface OH's which most likely participate in the adsorption of oxygen from the gas phase or mobilization of oxygen and CO on the surface. In contrast, during oxidation regeneration only CO₂ was desorbed and the surface OH's were not increased. Under our conditions, the reduction regeneration would certainly reduce both gold and silver to their metallic form. However, due to the small difference between the activities after the two regeneration

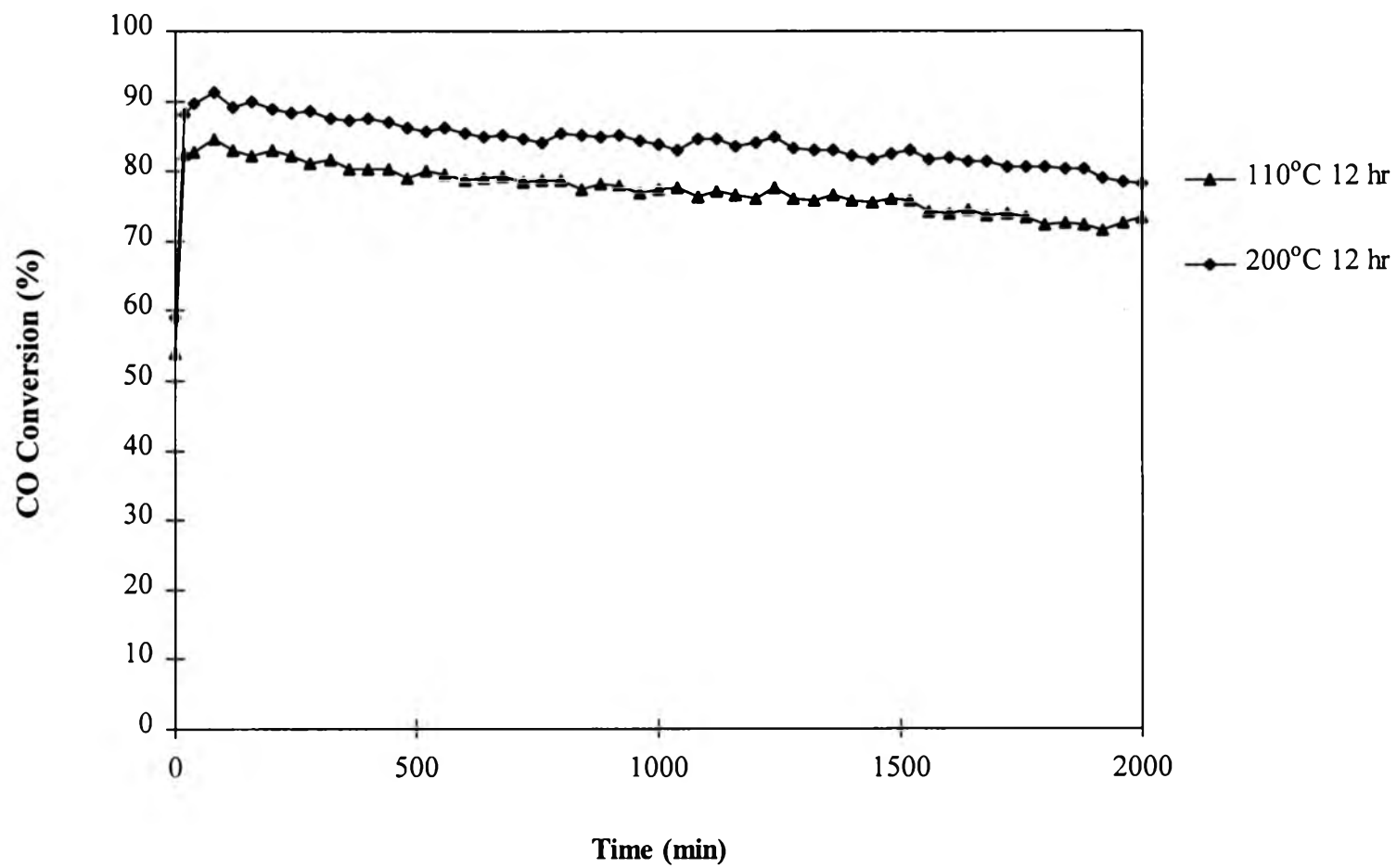


Figure 4.11 Reduction regeneration test of 0.1%Ag-Mn-Co at 50°C.

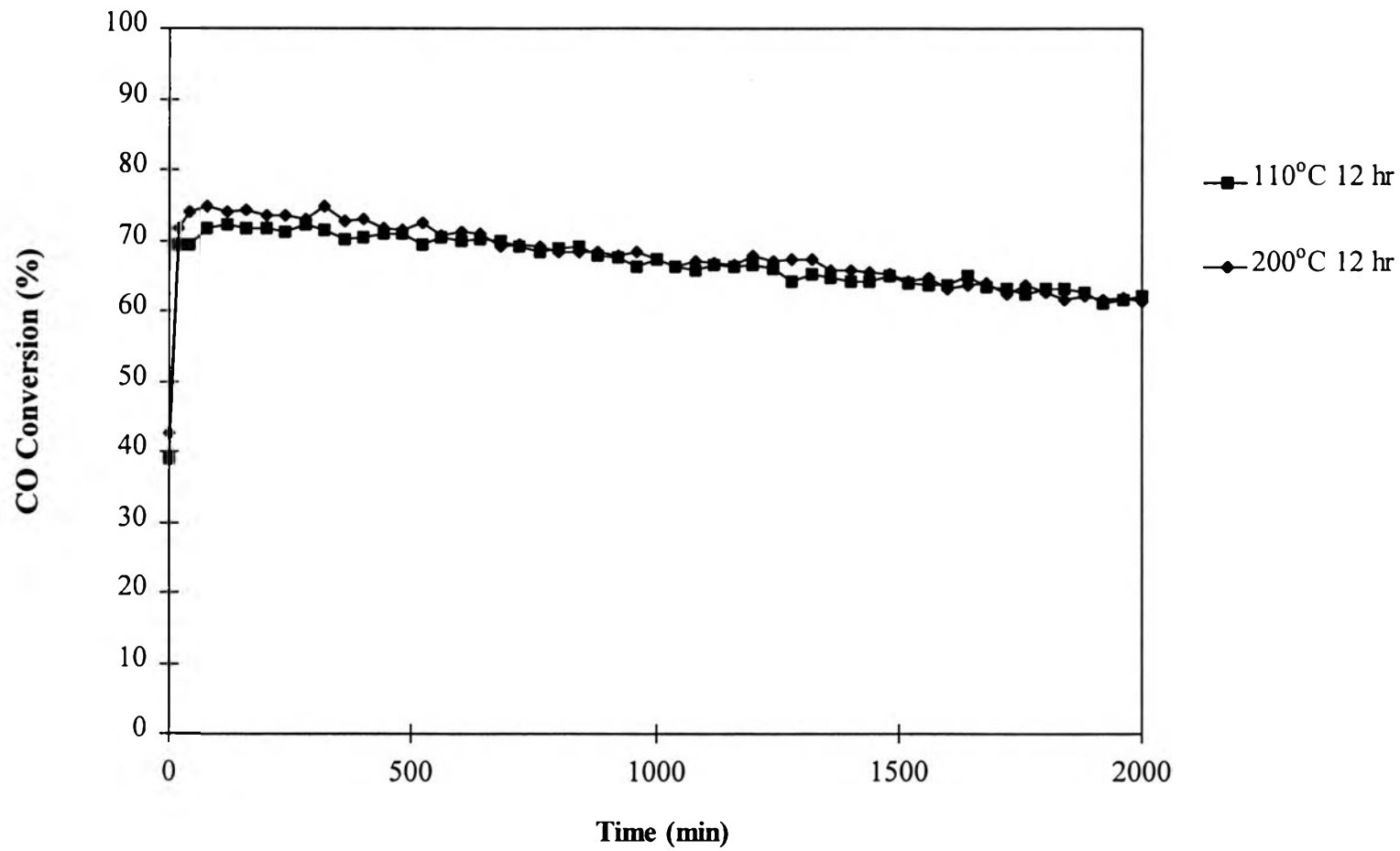


Figure 4.12 Reduction regeneration test of 0.1%Au-Mn-Co at 50°C.

experiments it was difficult to determine whether the metallic form or oxidic form of gold and silver were the better catalysts.

4.4 Effect of CO₂ Study

The excess CO₂ effect on the activity was studied. The catalytic behavior of silver and gold catalysts are illustrated in Figures 4.13 and 4.14, respectively. When 0.5% CO₂ was present in the reactant stream, the activity of both silver and gold catalyst immediately dropped from about 85% to 35% CO conversion. As soon as the CO₂ feed was cut off, the activity dramatically increased back to about 5% conversion less than original activity. There was excess CO₂ adsorption on the catalyst surface as non-reactive species. The retention of CO₂ led to the increase of surface coverage by intermediate species and decay of catalytic activity (Hoflund et al., 1995). The activity recovery after stopping CO₂ feed could possibly come from desorption or displacement by reactant gas of CO₂ from the surface. This gave back surface available for reaction. It was supported by Tanielyan and Augustine work (1992). They found that the oxygen could cause the expulsion of “CO₂-like” species from the surface. However, the activity from CO₂ environment could not be restored to the original activity.

We speculate that the drop in activity had two causes. First was physical blocking of the catalyst surface by weakly adsorbed CO₂. Second was carbonate formation due to the reaction between CO₂ and the support. The activity regeneration was primarily due to desorption of CO₂. The carbonates formed most likely did not decompose unless the temperature was raised to above 300°C.

Based on the faster recovery seen with the gold catalyst, after termination of CO₂ feed, we can conclude that CO₂ is more weakly bound to the gold catalyst.

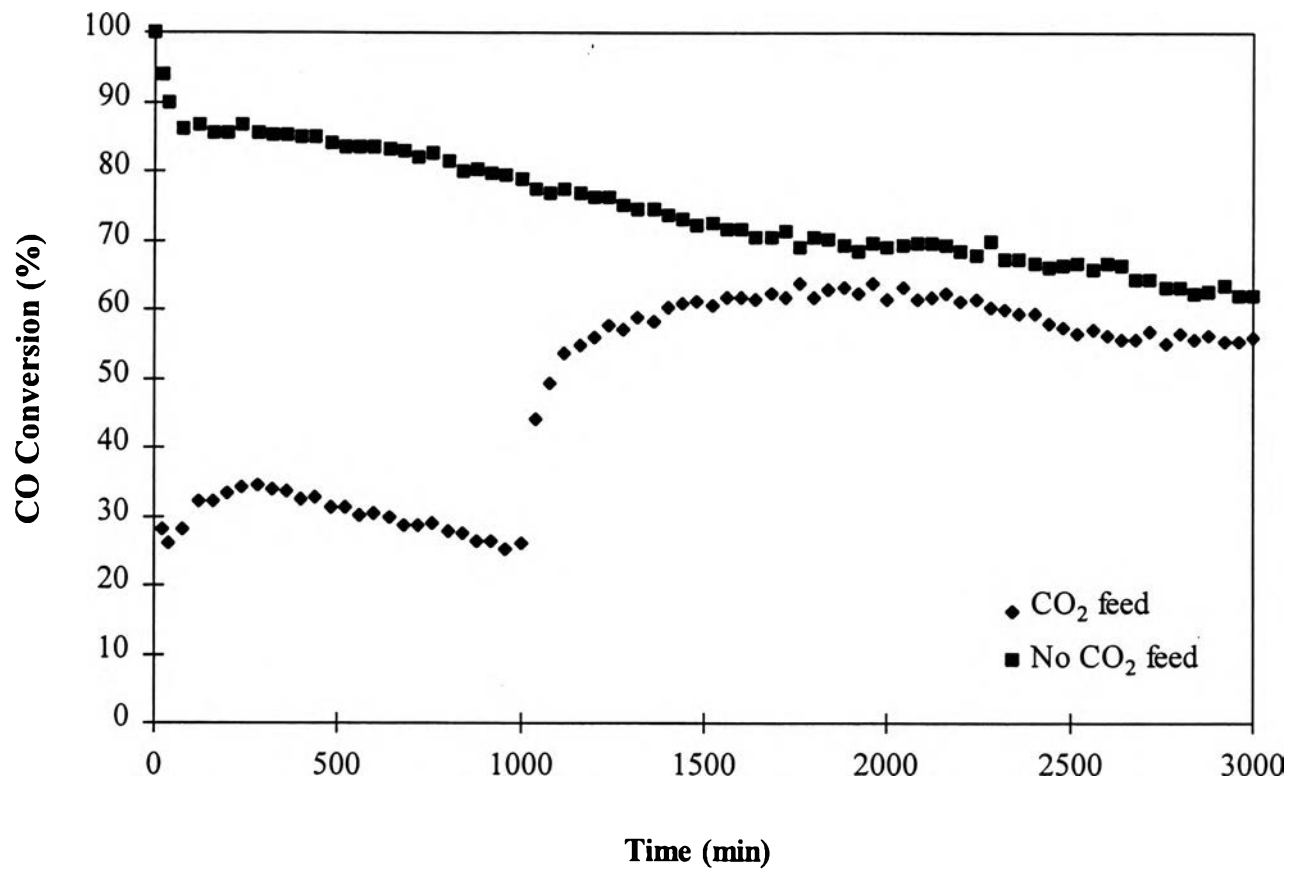


Figure 4.13 Effect of CO₂ on 0.1%Ag-Mn-Co at 50°C.

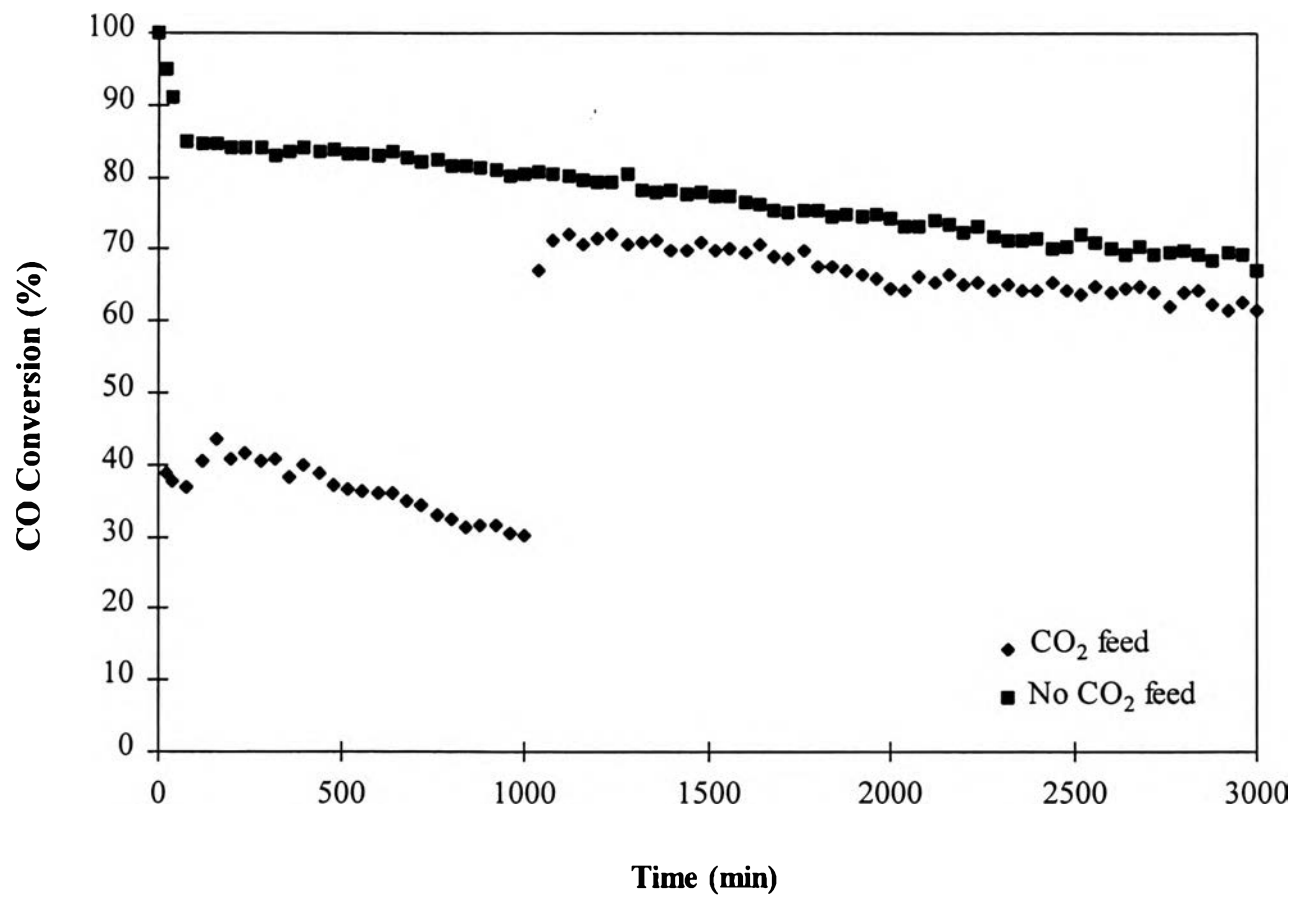


Figure 4.14 Effect of CO₂ on 0.1%Au-Mn-Co at 50°C.

4.5 Catalyst Characterization

In order to understand the behavior or deactivation scenario of our catalysts, physical and chemical property studies were necessary. BET surface area measurements, XRD, CHNS elemental analysis, TGA and TEM were employed to investigate the differences between active and deactivated catalysts. BET surface area and pore size measurements of fresh catalysts are shown in Tables 4.2 and 4.3, respectively. There were three types of supports for the catalysts, Mn oxide, Co oxide and Mn-Co oxide supports. The cobalt oxide support had higher surface area than Mn-Co and Mn supports, respectively. The higher surface areas of cobalt oxide supports led to the higher activity. Oxygen oxidation pretreated catalysts initially had less surface area than non-pretreated catalysts. However, they showed higher activity than non-pretreated catalysts perhaps due to activating the catalyst (Tanielyan and Augustine, 1992).

Tables 4.4, 4.5 and 4.6 show the comparisons of surface areas of catalysts at various conditions. Deactivated surface area of gold and silver catalyst were about the same as pretreated catalyst. So deactivation did not decrease the BET surface area.

Phase identification from X-ray diffraction is reported in Table 4.7. MnCO_3 form was reduced by oxidation pretreatment whereas Co_3O_4 form was increased. The comparison of silver and gold catalyst spectra at different environments are shown in Figures 4.15 and 4.16, respectively. The amount of metallic silver and gold in the catalysts decreased after pretreatment. These metallic forms might be changed to another oxide forms but they were not observed. This was most likely due to overlap of the oxide peaks with the supported peaks. In terms of the XRD spectra, there was no difference between the deactivated and fresh catalysts.

Table 4.4 Comparison of the surface area of 0.1%Ag-Mn-Co at various conditions

Catalyst environment	Surface area (m ² /g)
Non-pretreated catalyst	157.80
Oxidation pretreated catalyst	142.00
Deactivated catalyst	150.20

Table 4.5 Comparison of the surface area of 0.1%Au-Mn-Co at various conditions

Catalyst environment	Surface area (m ² /g)
Non-pretreated catalyst	190.10
Oxidation pretreated catalyst	148.70
Deactivated catalyst	149.00

Table 4.6 Comparison of the surface area of Mn-Co at various conditions

Catalyst environment	Surface area (m ² /g)
Non-pretreated catalyst	200.50
Oxidation pretreated catalyst	145.60
Deactivated catalyst	192.30

Table 4.7 Phase identification of catalysts

Catalyst	Non-pretreated	Oxidation pretreated
0.1%Ag-Mn	Ag Mn ₃ O ₄ , MnCO ₃	↓Ag Mn ₃ O ₄ , MnCO ₃ ↓
0.1%Ag-Mn-Co	Ag, Co ₃ O ₄ MnO _{1.88} , MnCO ₃	↓ Ag, Co ₃ O ₄ ↑ ↓ MnO _{1.88} , MnCO ₃ ↓
0.1%Au-Co	Au Co ₃ O ₄ , CoO	↓ Au ↑ Co ₃ O ₄ , CoO ↓
0.1%Au-Mn	Au Mn ₃ O ₄ , MnCO ₃	↓ Au Mn ₃ O ₄ , MnCO ₃ ↓
0.1%Au-Mn-Co	Au, Co ₃ O ₄ MnO _{1.88} , MnCO ₃	↓ Au, Co ₃ O ₄ ↑ ↓ MnO _{1.88} , MnCO ₃ ↓
Mn-Co	Co ₃ O ₄ MnO _{1.88} , MnCO ₃	-

Note : The results of oxidation pretreated catalyst were compared with non-pretreated catalyst.

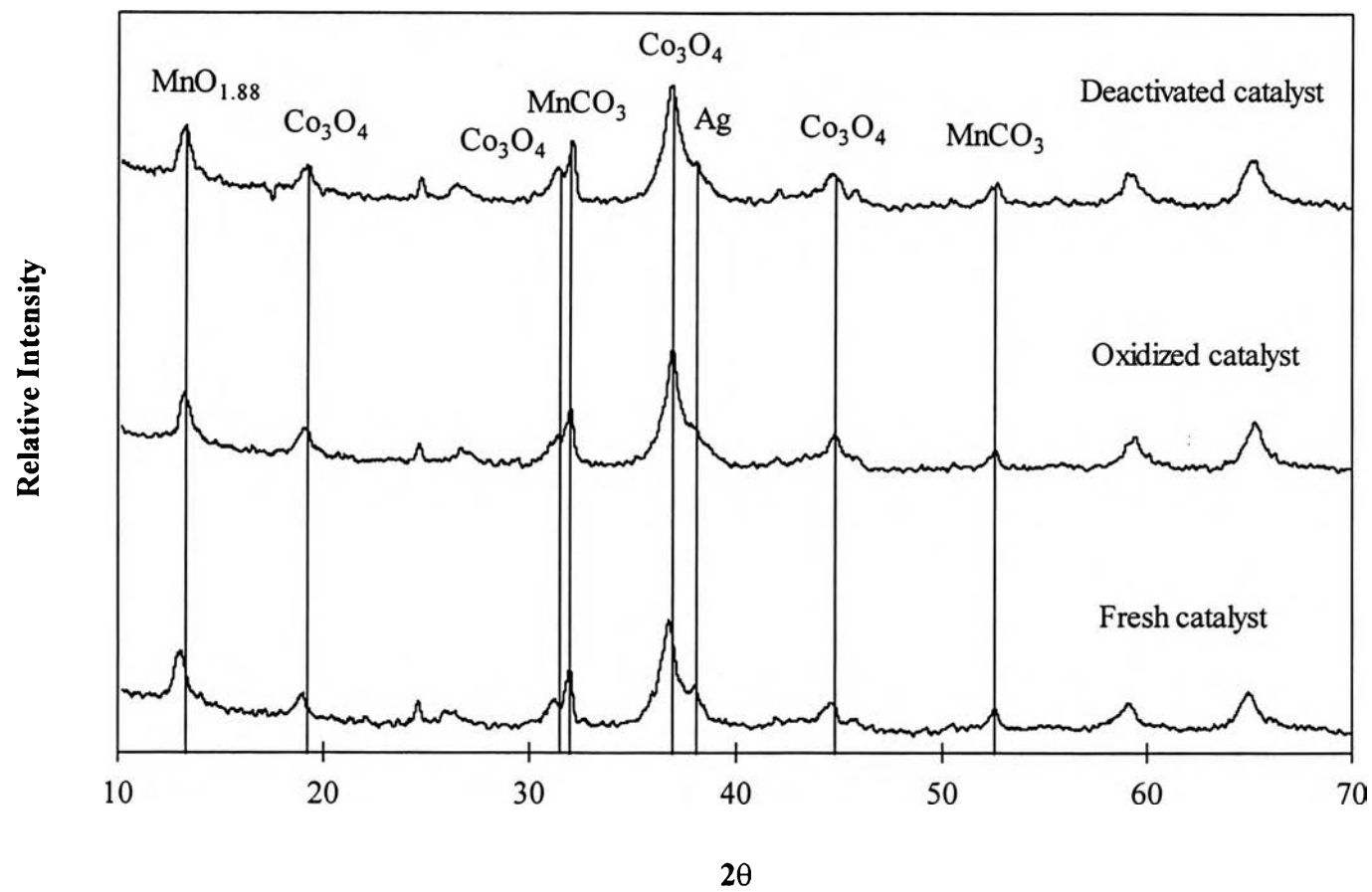


Figure 4.15 X-ray spectra of 0.1%Ag-Mn-Co.

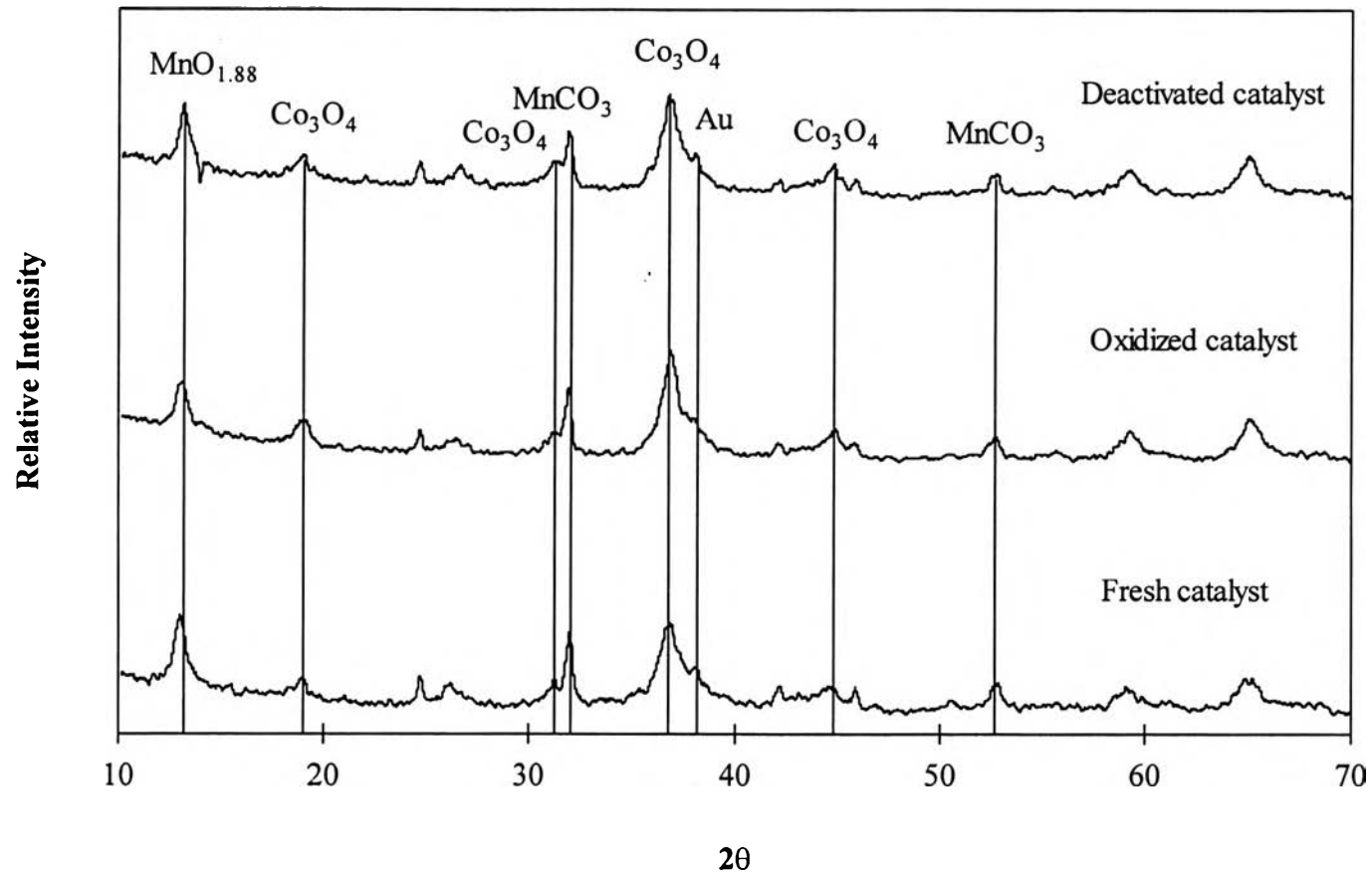


Figure 4.16 X-ray spectra of 0.1% Au-Mn-Co.

Figures 4.17 and 4.18 illustrated the changes in the XRD spectra due to oxidation regeneration of silver and gold catalysts, respectively. As the regeneration temperature increases, $\text{MnO}_{1.88}$ and MnCO_3 decrease while Co_3O_4 increases. The changes after reduction regeneration of silver and gold catalysts are shown in Figures 4.19 and 4.20, respectively. Reduction regeneration reduces the $\text{MnO}_{1.88}$ and Co_3O_4 phases in the catalysts.

In order to prove that there was carbonaceous species deposited on the catalyst surface, elemental analysis was carried out to measure the amount of carbon on the catalyst. Table 4.8 reports the amount of carbon on the catalyst in weight percent. Both deactivated silver and gold catalysts had higher amount of carbon than fresh catalysts, most likely in the form of carbonate.

Thermal gravimetric analysis was employed to determine the thermal stability of catalysts. Thermograms are shown in Figure 4.21. All three thermograms have the same features : An initial rapid weight loss below 100°C most likely due to desorption of weakly absorbed water and CO_2 . There is the weight loss at ~ 250 and 375°C , respectively. We believe these are due to decompose of the carbonate incorporated into the catalyst. The addition of gold and silver accelerates the weight loss perhaps through a catalytic effect.

High resolution TEM pictures of the catalysts are shown in Figures 4.22 and 4.23. We see that the coprecipitate catalyst particles are mostly uniform and have diameters of about $1.5 \mu\text{m}$. The high resolution did not allow for observation of the metals on the catalyst.

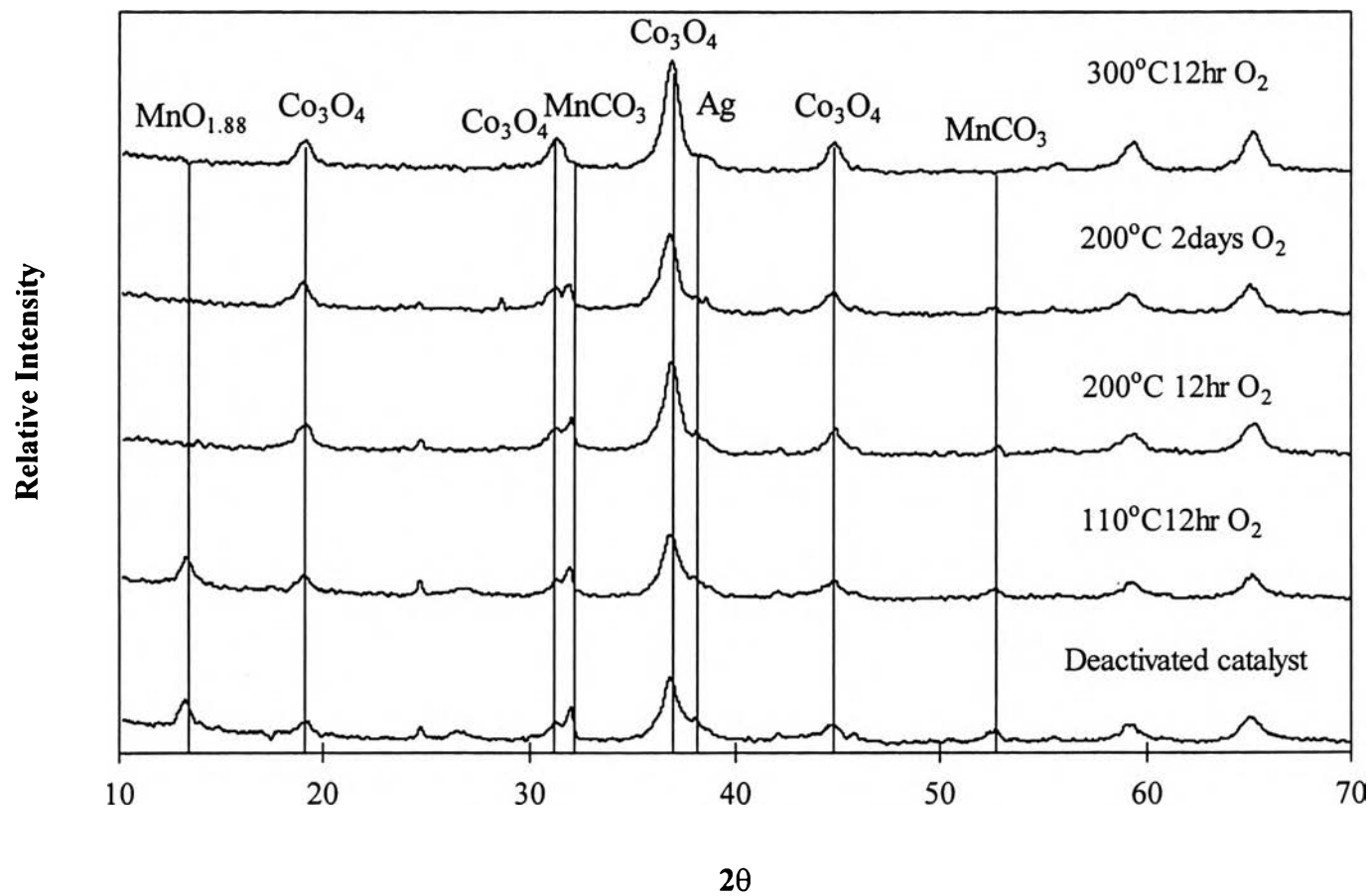


Figure 4.17 X-ray spectra of oxidation regenerated 0.1%Ag-Mn-Co.

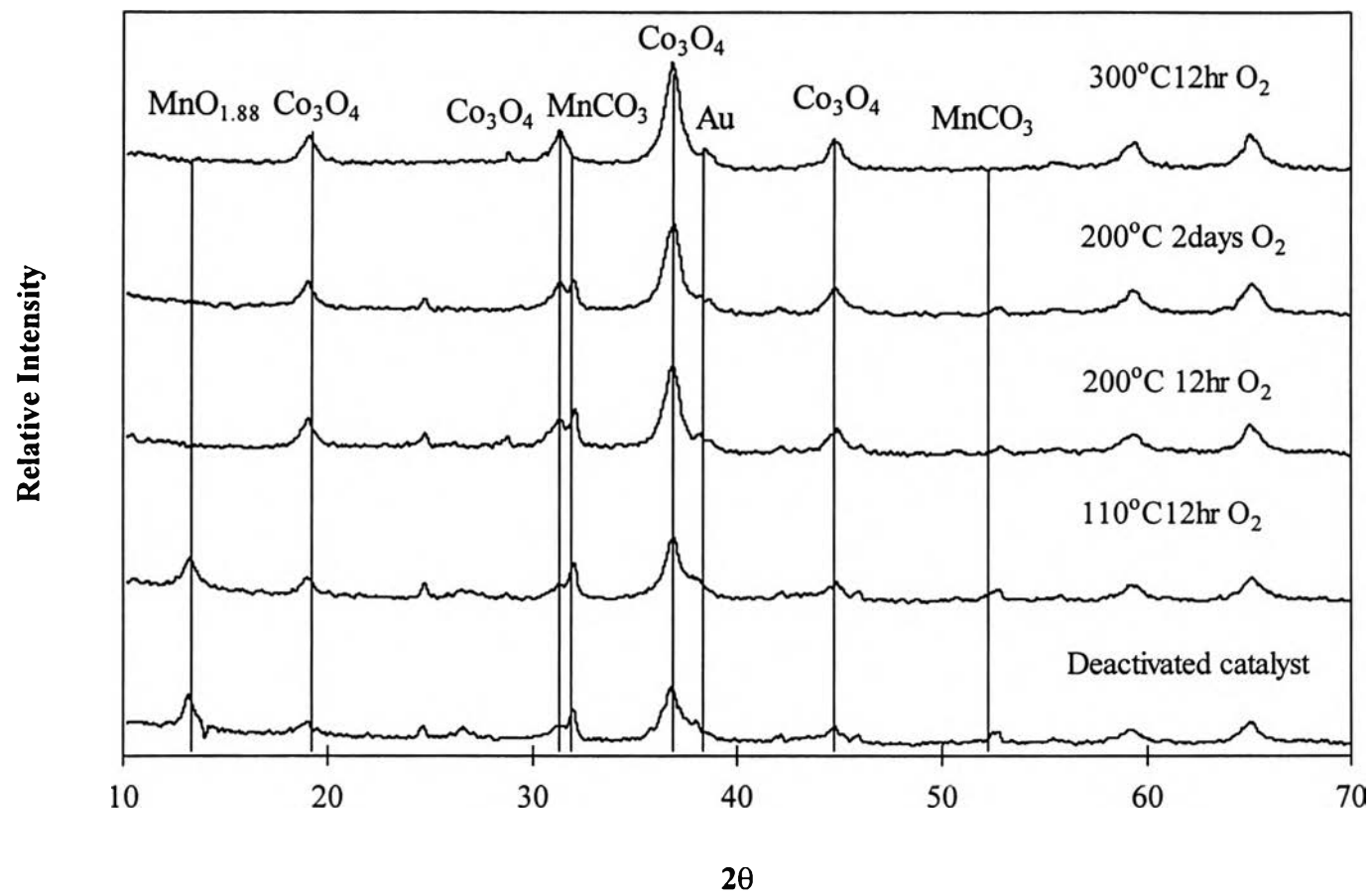


Figure 4.18 X-ray spectra of oxidation regenerated 0.1% Au-Mn-Co.

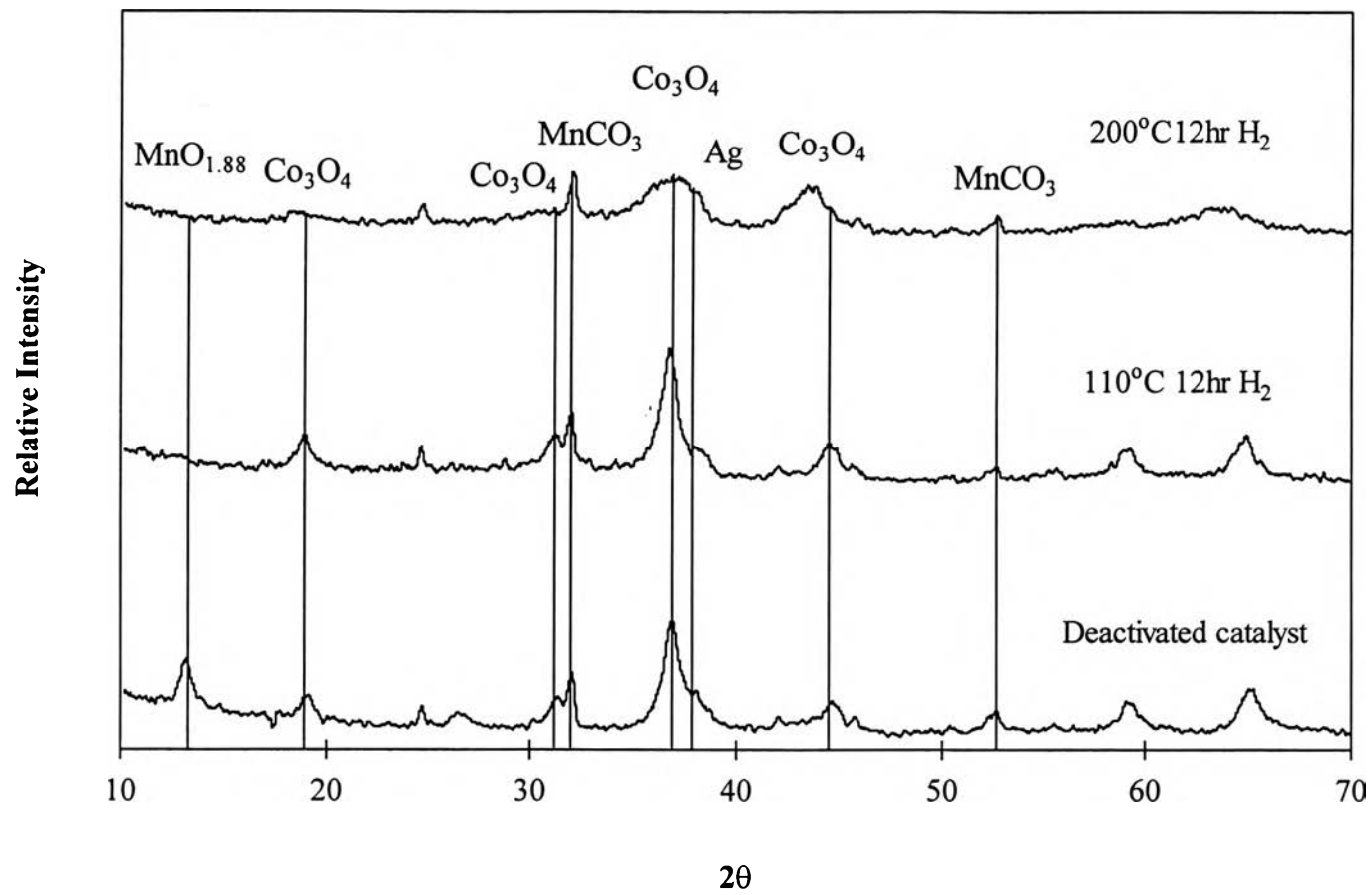


Figure 4.19 X-ray spectra of reduction regenerated 0.1%Ag-Mn-Co.

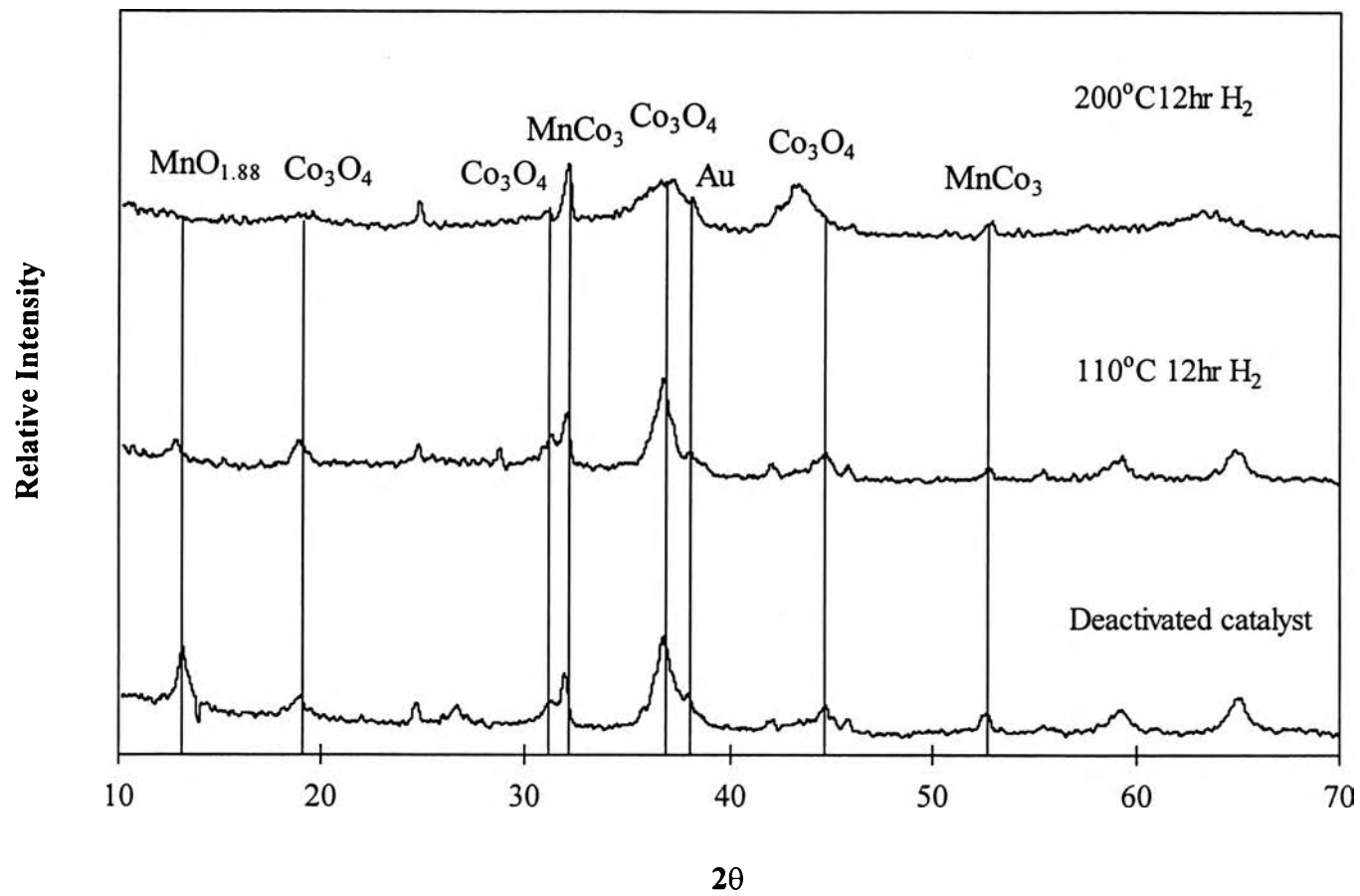


Figure 4.20 X-ray spectra of reduction regenerated 0.1% Au-Mn-Co.

Table 4.8 Comparison of amount of carbon on the catalyst

Catalyst	Amount of carbon (wt%)
Fresh 0.1%Ag-Mn-Co	1.76
0.1g deactivated 0.1%Ag-Mn-Co at 60°C	2.17
0.2g deactivated 0.1%Ag-Mn-Co at 60°C	1.86
Fresh 0.1%Au-Mn-Co	2.20
0.1g deactivated 0.1%Au-Mn-Co at 60°C	2.67
0.2g deactivated 0.1%Au-Mn-Co at 60°C	2.40

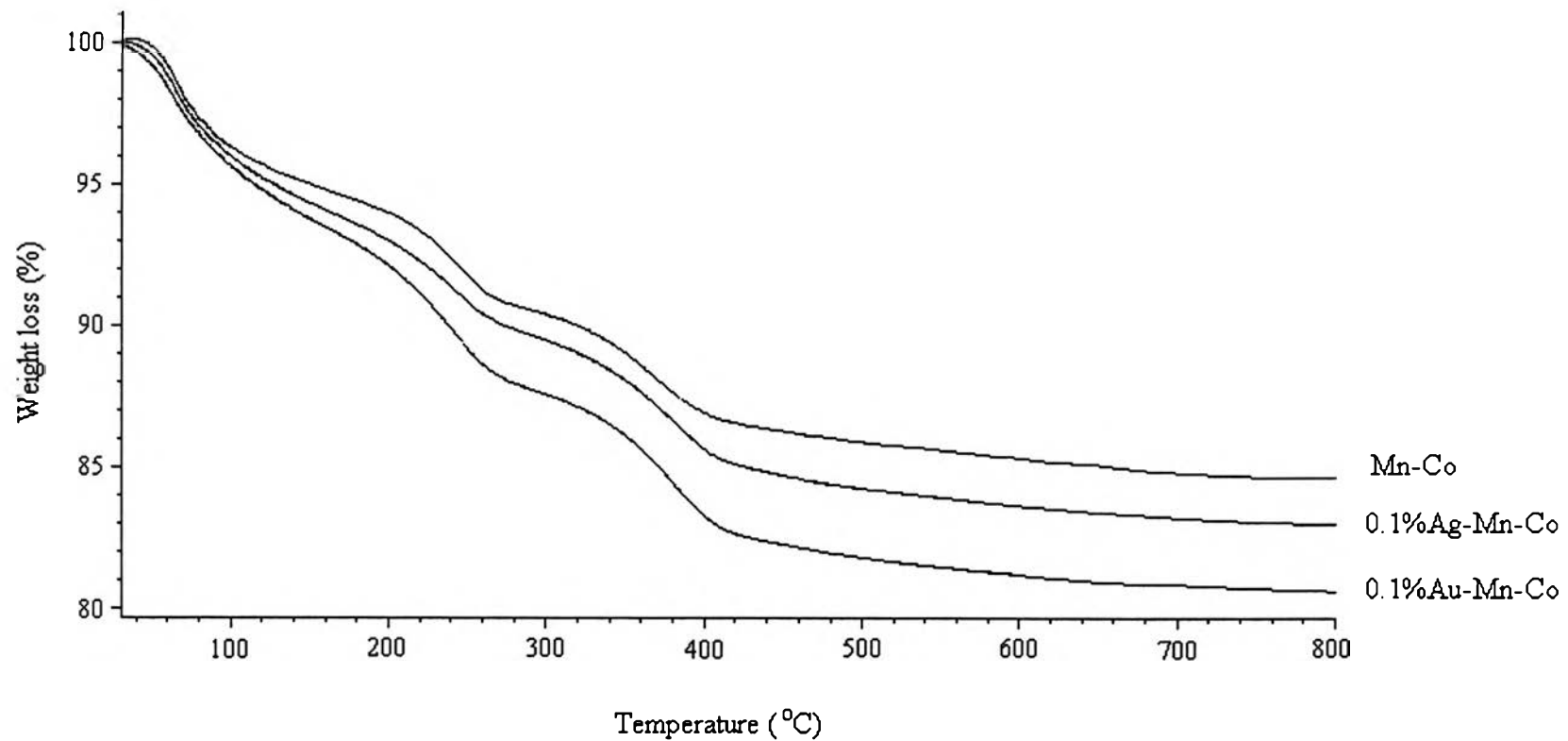


Figure 4.21 Thermogram of Mn-Co supported catalysts under nitrogen environment.

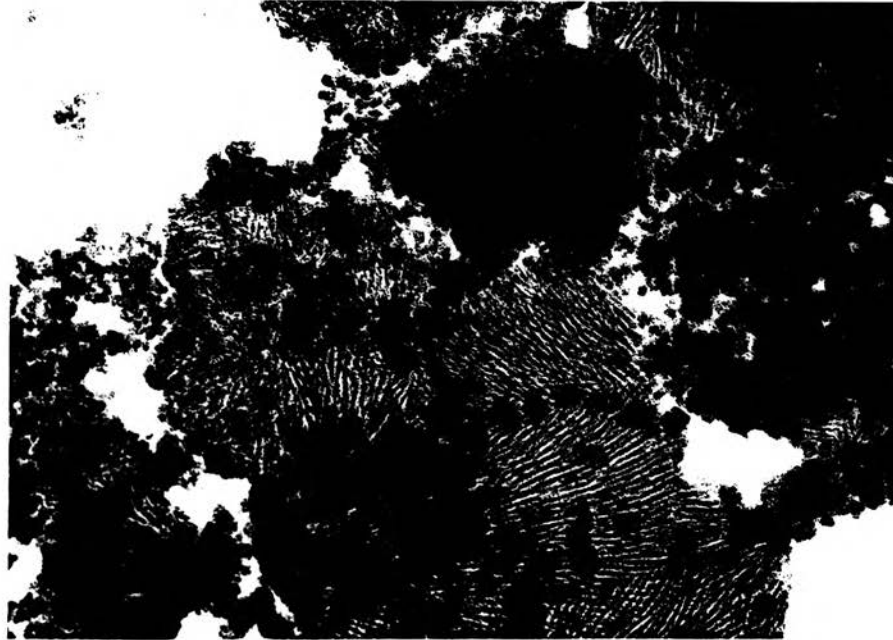


Figure 4.22 TEM micrograph of fresh 0.1%Ag-Mn-Co (Magnification : x 100K).

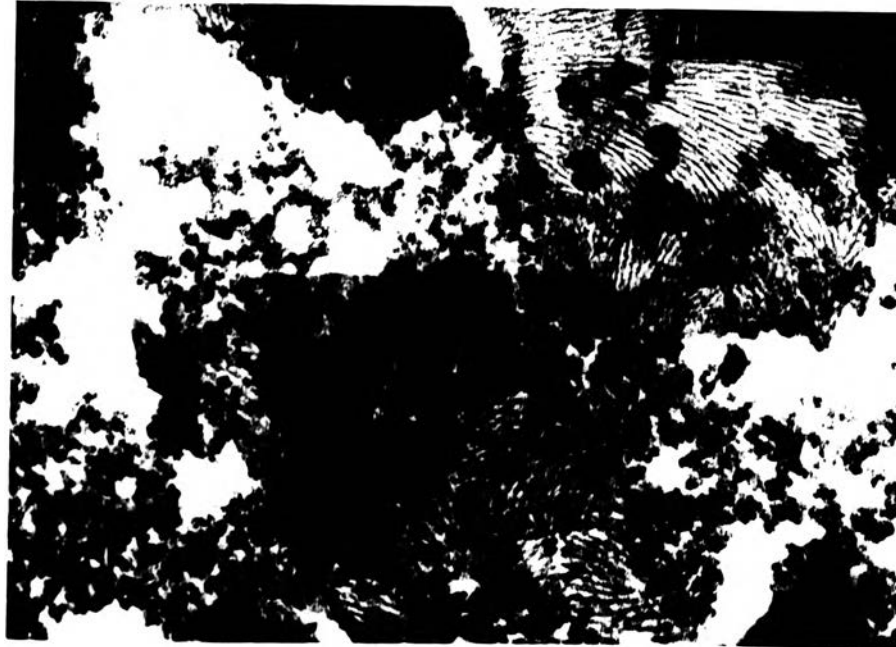


Figure 4.23 TEM micrograph of fresh 0.1%Au-Mn-Co (Magnification : x100K).