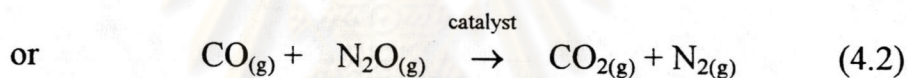


CHAPTER IV

RESULTS AND DISCUSSION

Catalytic oxidation reactions of carbon monoxide were performed using oxygen and nitrous oxide gases as oxidants and selected transition metal oxides as catalysts. The chemical equations which represent for the studied reactions are :



The catalysts used in this study are tricobalt tetraoxide (Co_3O_4), trimanganese tetraoxide (Mn_3O_4), ferric oxide (Fe_2O_3) and chromic oxide (Cr_2O_3). The physical properties such as thermal stability, BET surface area, as well as X-ray powdered diffraction of all four catalysts were determined.

Physical Characterization of the Catalysts

1. Thermal Stability

The thermal stability of the catalysts were determined by using thermal gravimetry (TG) and differential thermal analysis (DTA). TG and DTA thermograms of Co_3O_4 , Mn_3O_4 , Fe_2O_3 and Cr_2O_3 are shown in Figure 4.1, 4.2, 4.3 and 4.4, respectively. Figure 4.1 shows that there is no significant weight loss of Co_3O_4 upon heating from 40°C to almost 800°C . A small weight loss at

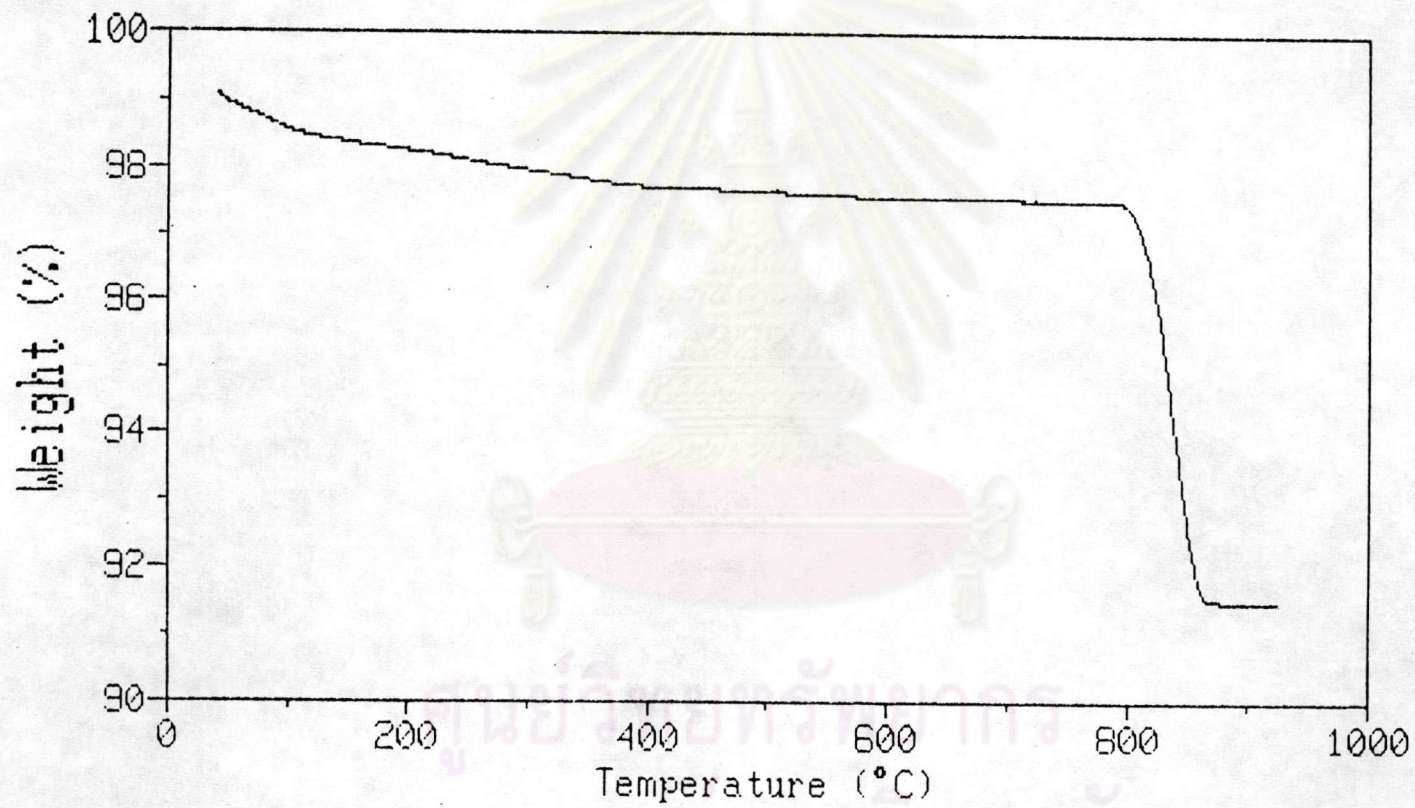


Figure 4.1 TG thermogram of Co_3O_4

a lower temperature range is accounted for desorption of moisture from Co_3O_4 material. A sharp weight loss at 800°C indicates a phase transformation of Co_3O_4 that loss O_2 to form CoO (40). This shows that the Co_3O_4 catalyst is thermally stable up to about 800°C .

Figure 4.2 shows a TG/DTA thermogram of the Fe_2O_3 catalyst. A weight loss from 40°C up to about 400°C from TG curve and a broad endothermic peak at the same temperature range of DTA curve are due to a desorption of moisture from the Fe_2O_3 material. There is a noise at 500°C . This result indicates that the Fe_2O_3 catalyst is very stable within the temperature range of 40°C to 900°C .

Figure 4.3 shows a TG/DTA thermogram of the Mn_3O_4 catalyst. A weight loss from 40°C up to about 420°C in TG curve and a broad endothermic peak at about 490°C of DTA curve are due to a slow desorption of moisture from the Mn_3O_4 material. There is an increase in weight from 450°C to 750°C in TG curve but there is no change in DTA curve. A weight loss from 750°C to 820°C in TG curve and a sharp exothermic peak at 800°C of DTA curve show a phase transformation of Mn_3O_4 . By heating over 750°C , the new phase of manganese decomposes to another different phase. Thus, Mn_3O_4 is not stable upon heating over 750°C . The new phase formed at about 800°C is thermally stable up to 820°C .

Figure 4.4 shows a TG/DTA thermogram of the Cr_2O_3 catalyst. From TG curve, there is a weight loss from 40°C up to 560°C and an increase in weight over 620°C . Three broad exothermic peaks at about $370, 450$ and 850°C . In DTA curve show phase transformations. They indicate that the Cr_2O_3 catalyst has three phase transformation changes over 370°C . Therefore, Cr_2O_3

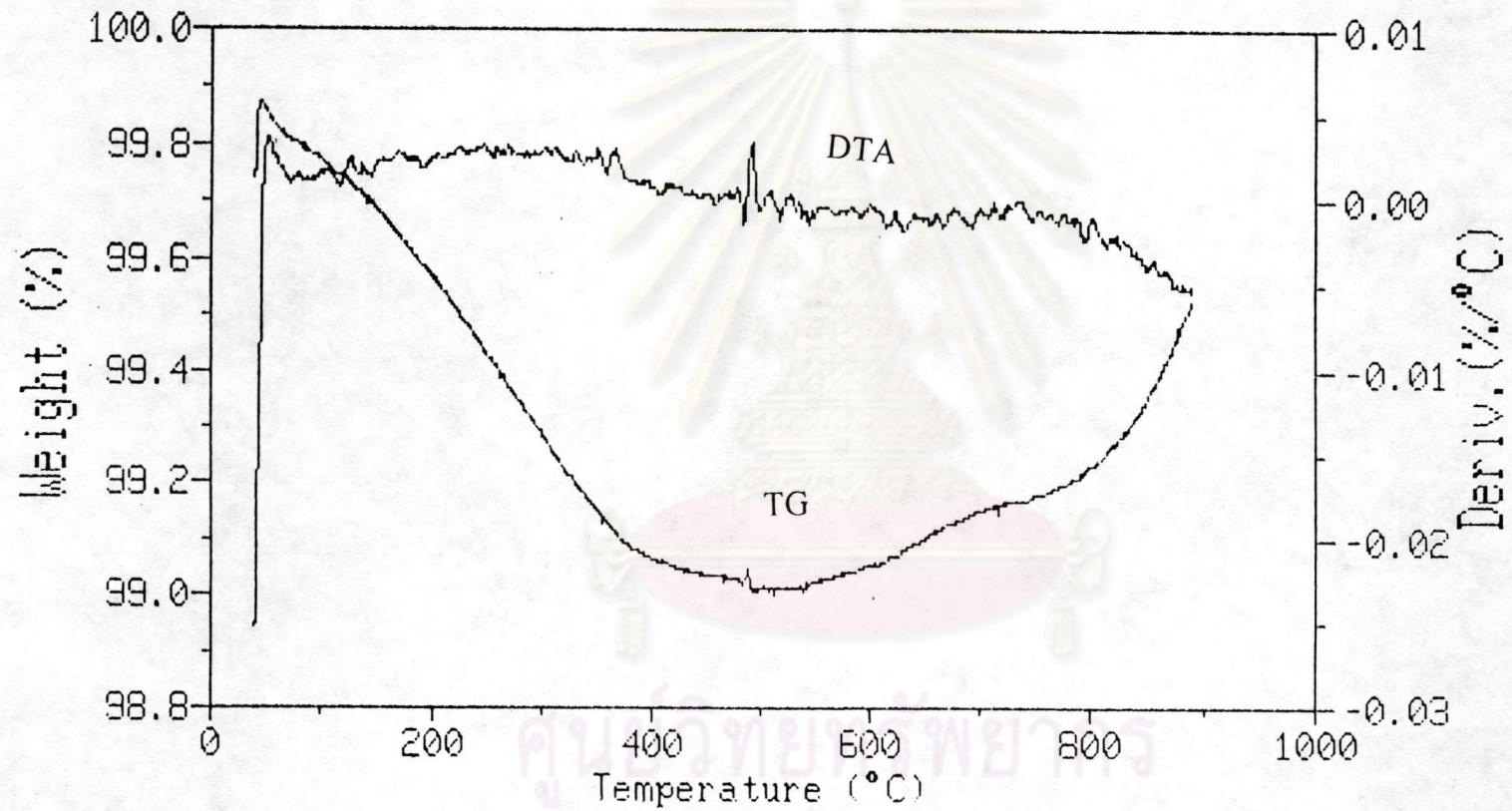


Figure 4.2 TG/DTA thermogram of Fe_2O_3

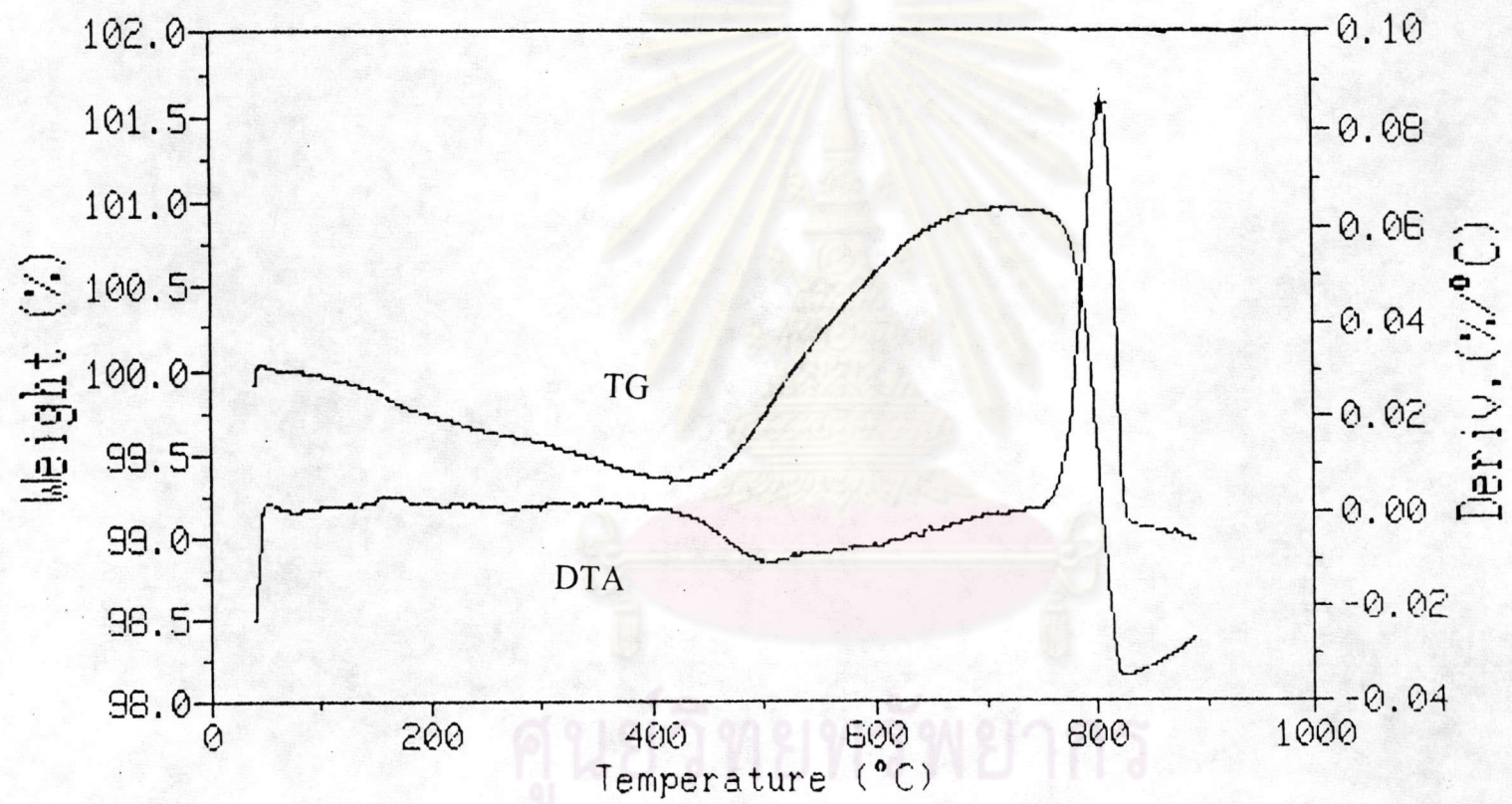


Figure 4.3 TG/DTA thermogram of Mn_3O_4

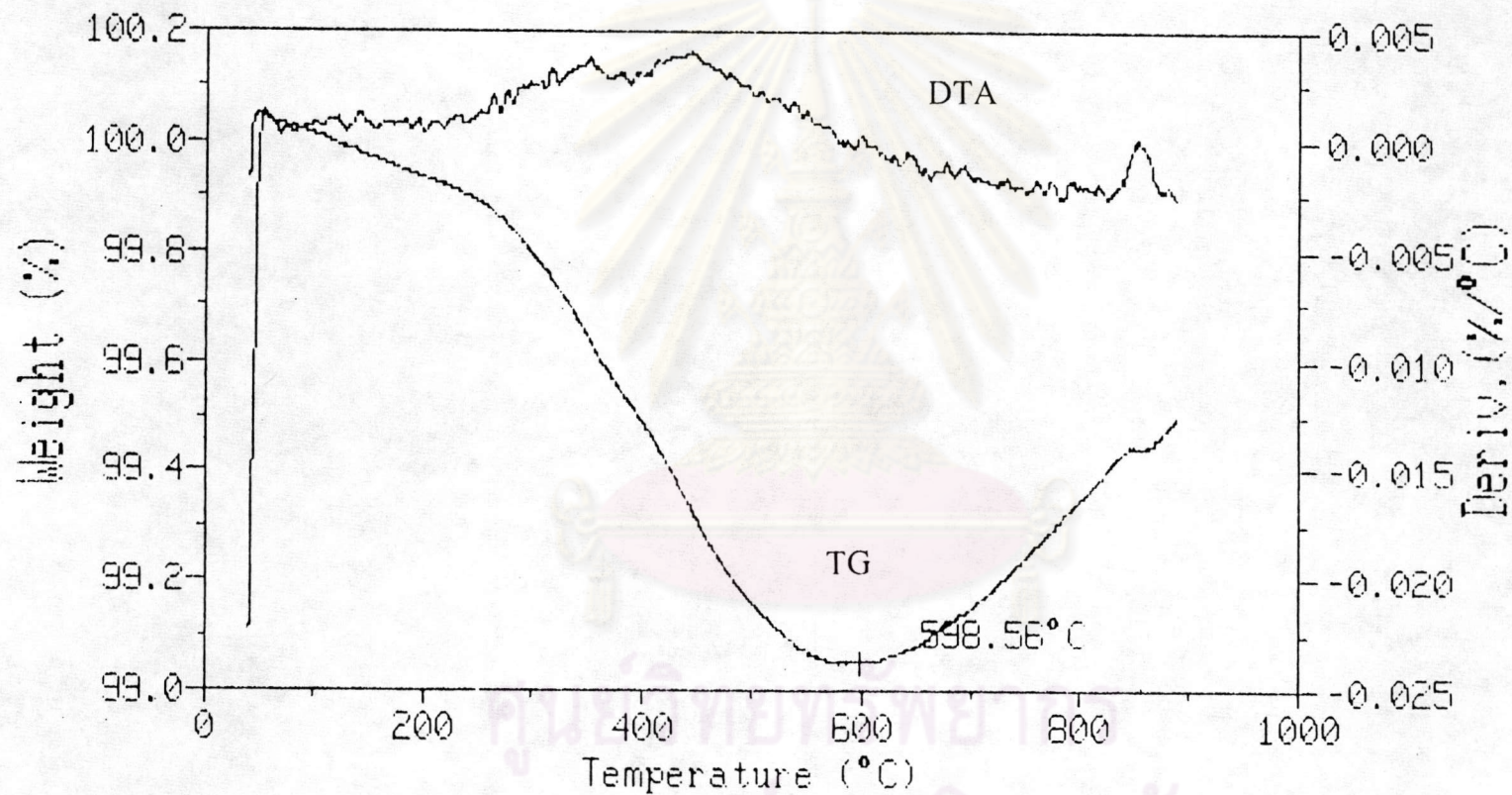
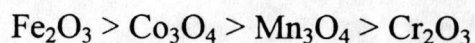


Figure 4.4 TG/DTA thermogram of Cr_2O_3

is the least thermally stable catalyst among those used in this work. The thermal stability of those catalysts are in the following order:



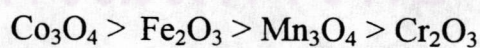
2. BET Surface Area

The surface of the catalysts were measured by BET method. The BET surface area of the catalysts are shown in Table 4.1.

Table 4.1 BET surface area of the Co_3O_4 , Fe_2O_3 , Mn_3O_4 and Cr_2O_3 catalysts

Catalyst	BET Surface Area (m^2/g)
Co_3O_4	17.50
Fe_2O_3	10.74
Mn_3O_4	5.98
Cr_2O_3	2.61

Data in Table 4.1 show the surface area of catalysts in following order :



Typically, activity of a catalyst is proportional to its surface area. This information is useful for interpretation of the catalytic performance.

3. X-ray Powdered Diffraction

1) Co_3O_4 Catalyst

An X-ray diffraction (XRD) pattern of the Co_3O_4 catalyst is shown in Figure 4.5 and its XRD data is shown in Table 4.2. The XRD pattern matching between the Co_3O_4 catalyst sample and the reference (Co_3O_4) is shown in appendix (Figure A.1). Therefore, the Co_3O_4 catalyst has the same structure as the reference. The XRD pattern of used Co_3O_4 catalyst in the reaction of CO with N_2O and CO with O_2 comparing to the fresh catalyst and its reference confirm that the structure of catalyst does not change after being used.

Table 4.2 XRD data of the fresh Co_3O_4

D (Å°)	I/I _o
4.667	30
2.861	42
2.781	19
2.438	100
2.331	23
2.021	34
1.650	22
1.556	41
1.430	45
1.234	22

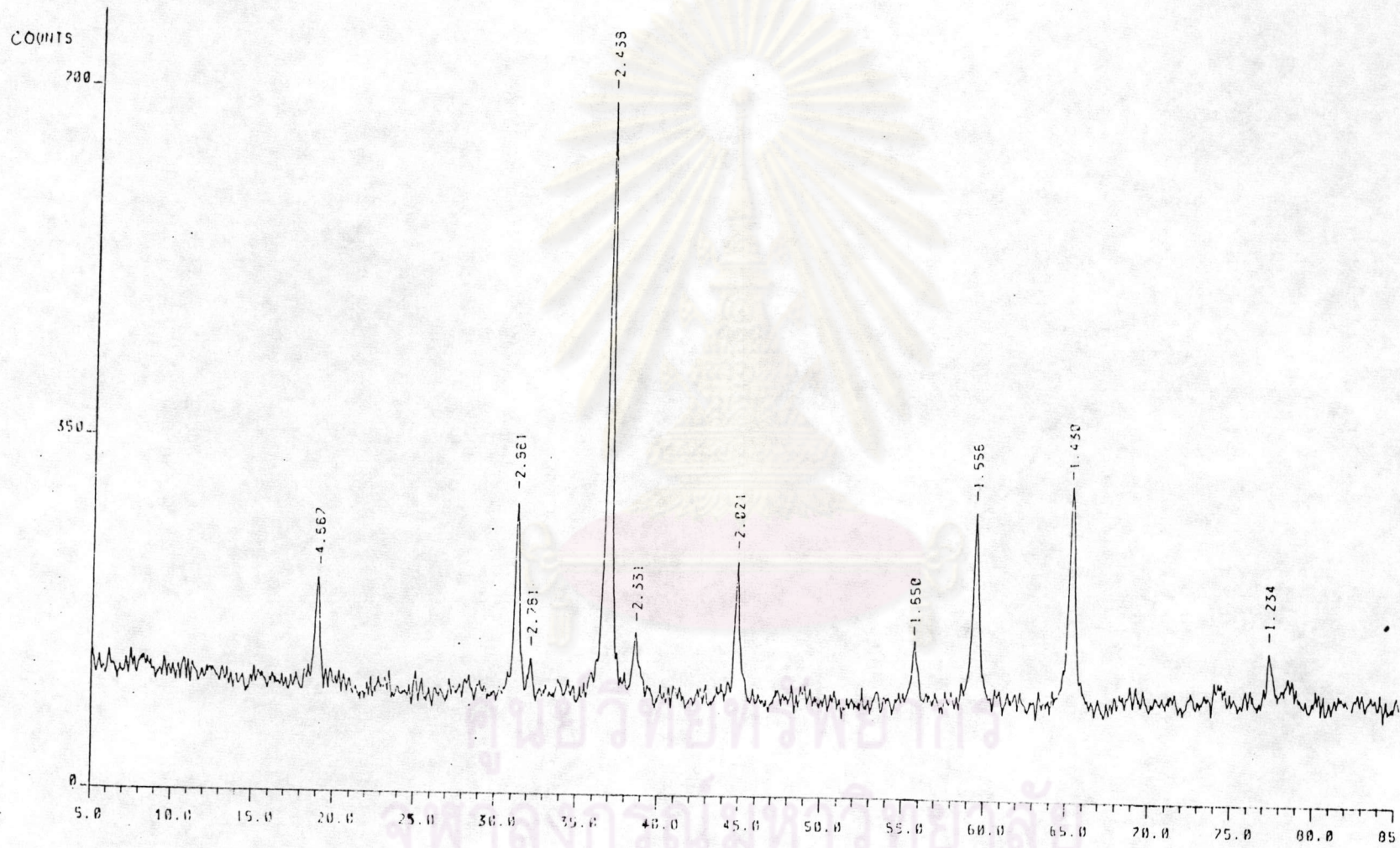


Figure 4.5 XRD pattern of the fresh Co_3O_4

2) Fe₂O₃ Catalyst

An X-ray diffraction (XRD) pattern of the Fe₂O₃ catalyst is shown in Figure 4.6 and its XRD data is shown in Table 4.3. The XRD pattern matching between the Fe₂O₃ catalyst sample and the reference (Fe₂O₃) is shown in appendix (Figure A.2). Therefore, the Fe₂O₃ catalyst has the same structure as the reference. The XRD pattern of used Fe₂O₃ catalyst in the reaction of CO with N₂O and CO with O₂ comparing to the fresh catalyst and its reference confirm that the structure of catalyst does not change after being used.

3) Mn₃O₄ Catalyst

An X-ray diffraction (XRD) pattern of the Mn₃O₄ catalyst is shown in Figure 4.7 and its XRD data is shown in Table 4.4. The XRD patterns of Mn₃O₄ catalyst sample comparing to the pattern of the reference (Mn₃O₄ and Mn₂O₃), as shown in appendix (Figure A.3) indicates that the sample is a mixture of Mn₃O₄ and Mn₂O₃. By comparison of peak at 36.08° and 32.92° of the sample with their individual baseline peaks, the ratio of Mn₃O₄:Mn₂O₃ is 1:1.7.

The XRD pattern of used Mn₃O₄ sample in the reaction of CO with N₂O, comparing to the fresh Mn₃O₄ catalyst and the Mn₃O₄ and Mn₂O₃ references. The XRD pattern of used Mn₃O₄ sample is different from the fresh catalyst as shown in Figure 4.7 (XRD data in Table 4.4) and Figure 4.8 (XRD data in Table 4.5), respectively. The XRD pattern matching between the used Mn₃O₄ sample with the Mn₃O₄ and Mn₂O₃ references, shown in appendix (Figure A.4) indicates that the Mn₃O₄:Mn₂O₃ ratio in the used

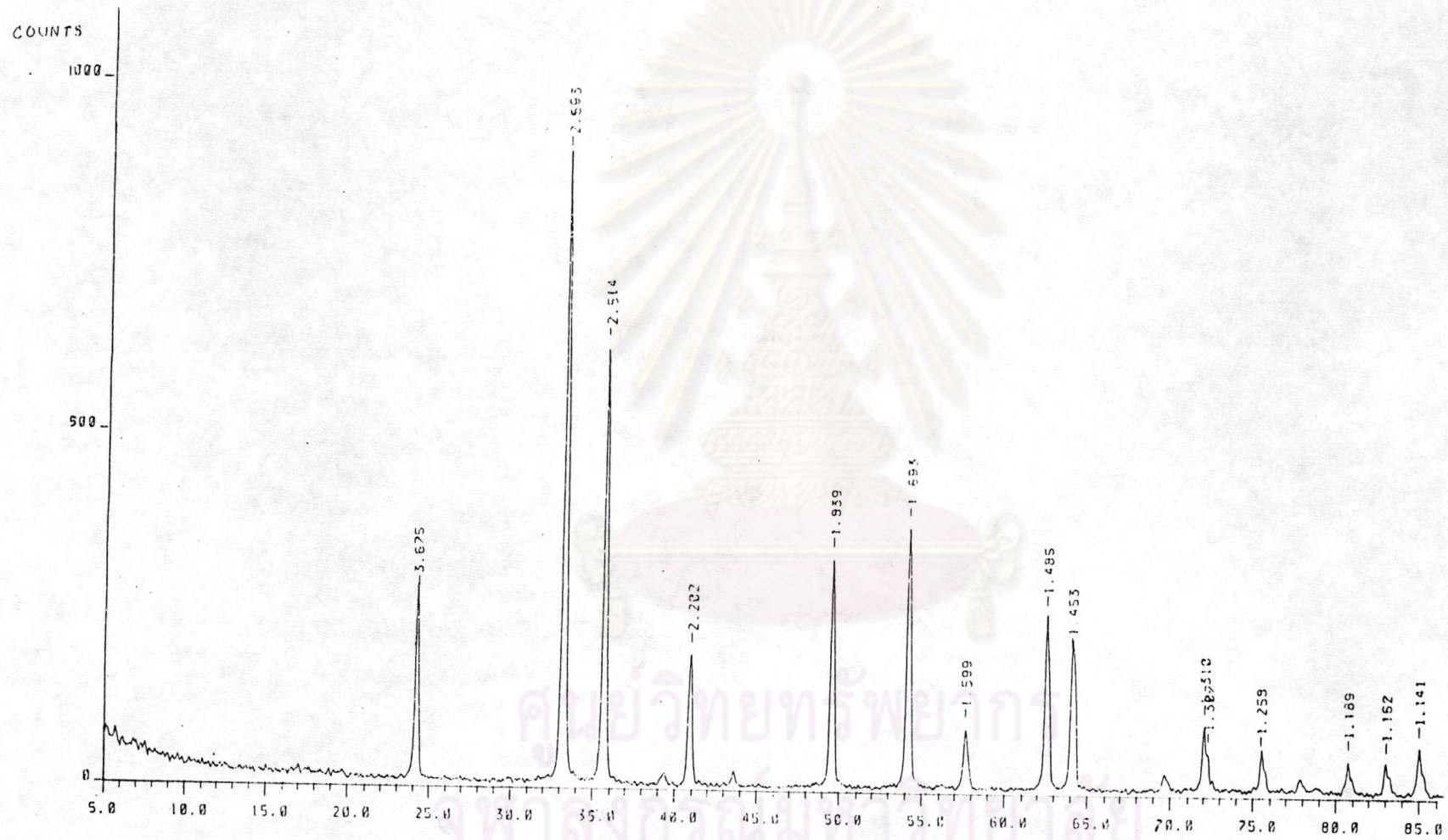


Figure 4.6 XRD pattern of the fresh Fe_2O_3

Table 4.3 XRD data of the fresh Fe₂O₃

D(A°)	I/I ₀
3.675	32
2.693	100
2.514	69
2.202	21
1.839	36
1.693	41
1.599	10
1.485	28
1.453	24
1.310	11
1.307	7
1.258	8
1.189	6
1.162	6
1.141	8
1.103	8

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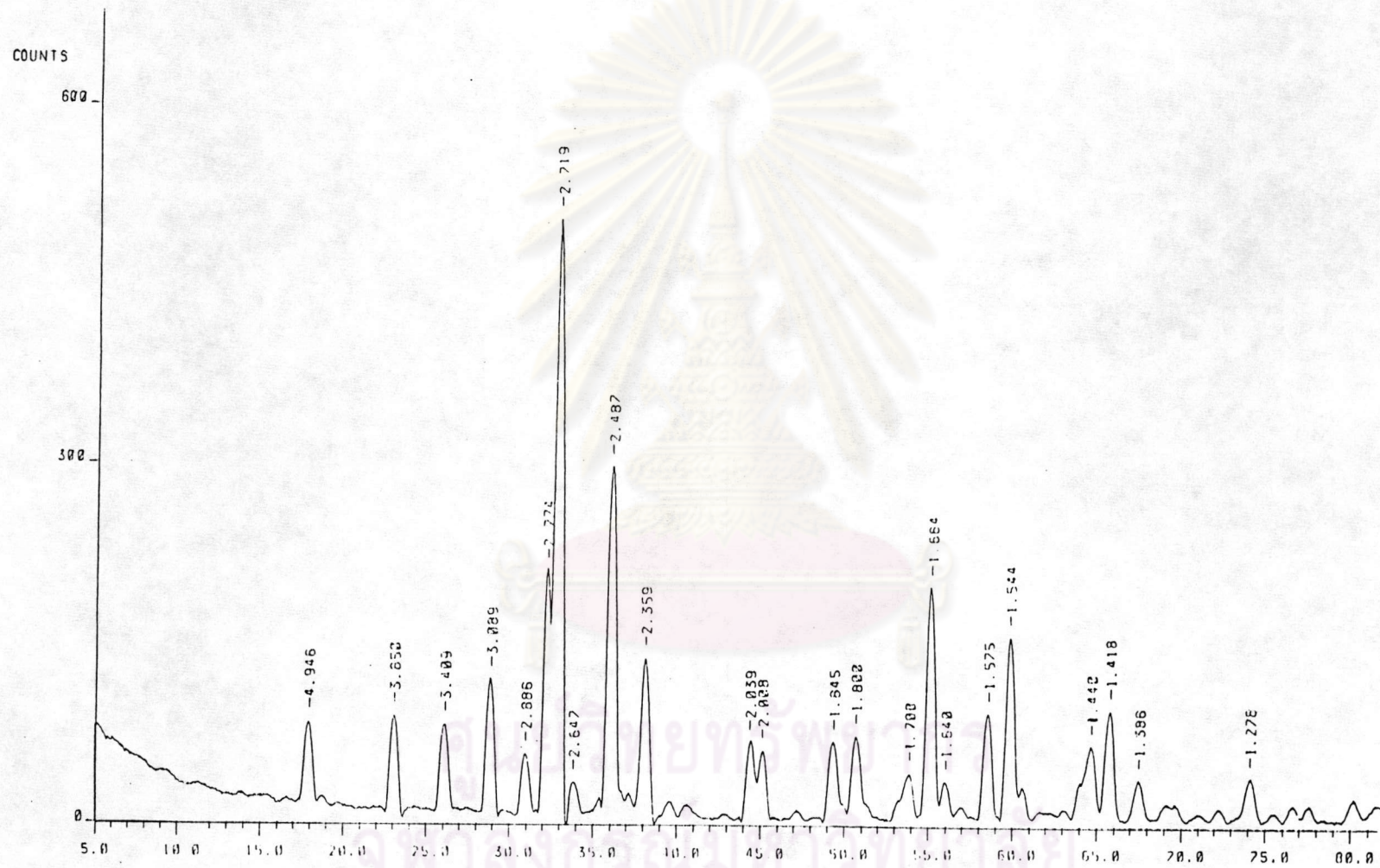


Figure 4.7 XRD pattern of the fresh Mn_3O_4

Table 4.4 XRD data of the fresh Mn₃O₄

D(A°)	I/I ₀
4.946	17
3.850	18
3.409	17
3.089	24
2.886	12
2.774	42
2.719	100
2.647	7
2.487	59
2.359	27
2.039	14
2.008	12
1.845	14
1.800	15
1.700	9
1.664	39
1.640	7
1.575	19
1.544	31
1.440	13
1.418	19
1.386	8
1.278	8
1.124	6

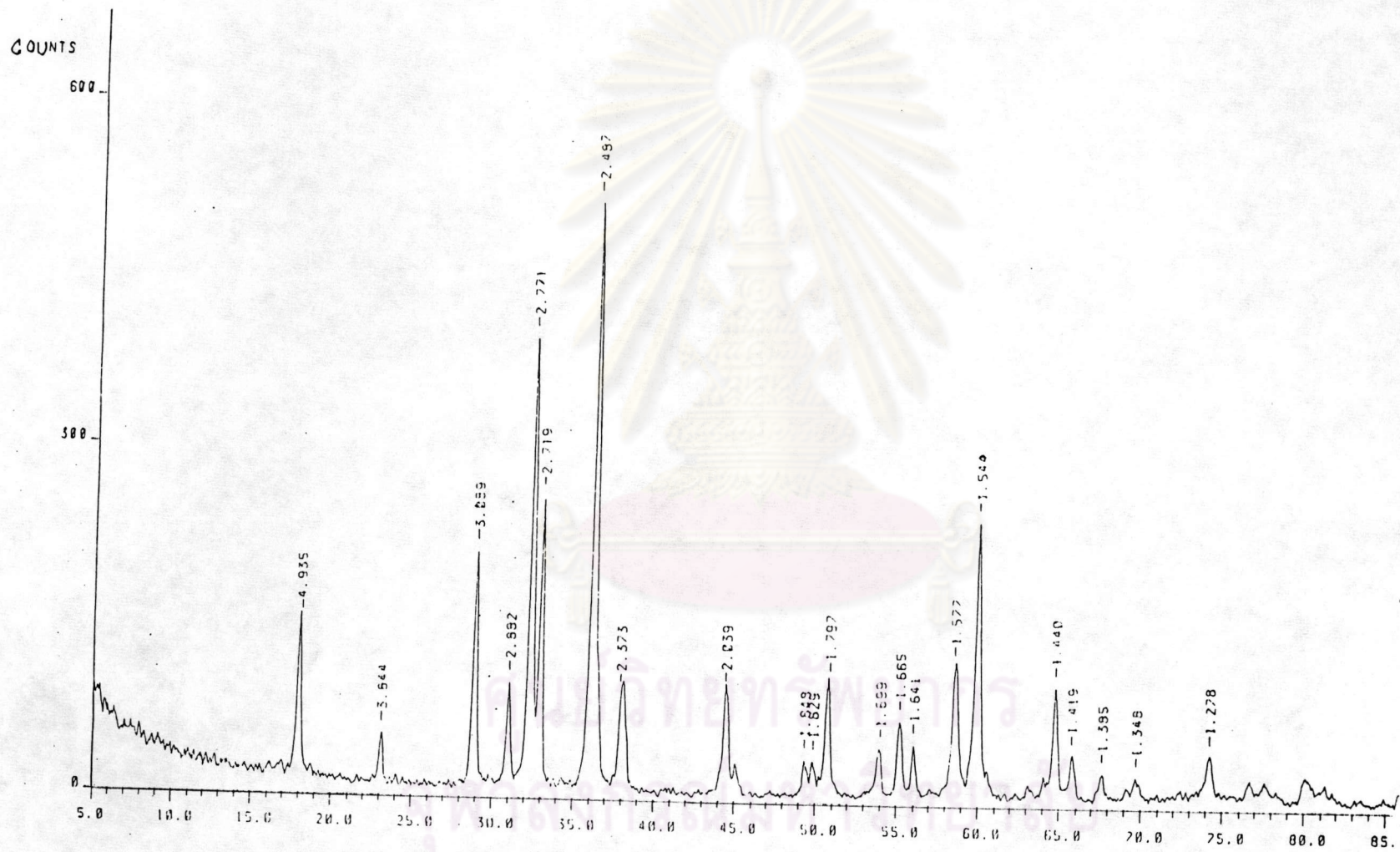


Figure 4.8 XRD pattern of the used Mn_3O_4 in the reaction of CO with N_2O

Table 4.5 XRD data of the used Mn_3O_4 in the reaction of CO with N_2O

D(A°)	I/I ₀
4.935	30
3.844	10
3.089	41
2.882	19
2.771	77
2.719	50
2.487	100
2.373	18
2.039	20
1.848	7
1.829	7
1.797	20
1.699	9
1.665	14
1.641	10
1.557	23
1.544	48
1.440	20
1.419	9
1.385	6
1.348	5
1.278	9

is higher than the fresh catalyst; the evaluated $\text{Mn}_3\text{O}_4:\text{Mn}_2\text{O}_3$ ratio of used catalyst in this reaction is 2:1.

The XRD pattern of used Mn_3O_4 sample in the reaction of CO with O_2 , comparing to the fresh Mn_3O_4 catalyst and the Mn_3O_4 and Mn_2O_3 references. The XRD pattern of used Mn_3O_4 sample is different from the fresh catalyst as shown in Figure 4.7 (XRD data in Table 4.4) and Figure 4.9 (XRD data in Table 4.6), respectively. The XRD pattern matching between the used Mn_3O_4 sample with the Mn_3O_4 and Mn_2O_3 references, shown in appendix (Figure A.5) indicates that the $\text{Mn}_3\text{O}_4:\text{Mn}_2\text{O}_3$ ratio in the used catalyst is lower than the fresh catalyst; the evaluated $\text{Mn}_3\text{O}_4:\text{Mn}_2\text{O}_3$ ratio of used catalyst in this reaction is 1:3.6. The XRD pattern of used Mn_3O_4 catalyst in this reaction of CO with N_2O and CO with O_2 comparing to the fresh catalyst and their references confirm that the structure of catalyst change after being used.

4) Cr_2O_3 Catalyst

An X-ray diffraction (XRD) pattern of the Cr_2O_3 catalyst is shown in Figure 4.10 and its XRD data is shown in Table 4.7. The XRD pattern matching between the Cr_2O_3 catalyst sample and the reference (Cr_2O_3) is shown in appendix (Figure A.6). Therefore, the Cr_2O_3 sample has the same structure as the reference. The XRD pattern of used Cr_2O_3 catalyst in the reaction of CO with N_2O and CO with O_2 comparing to the fresh catalyst and its reference confirm that the structure of catalyst does not change after being used.

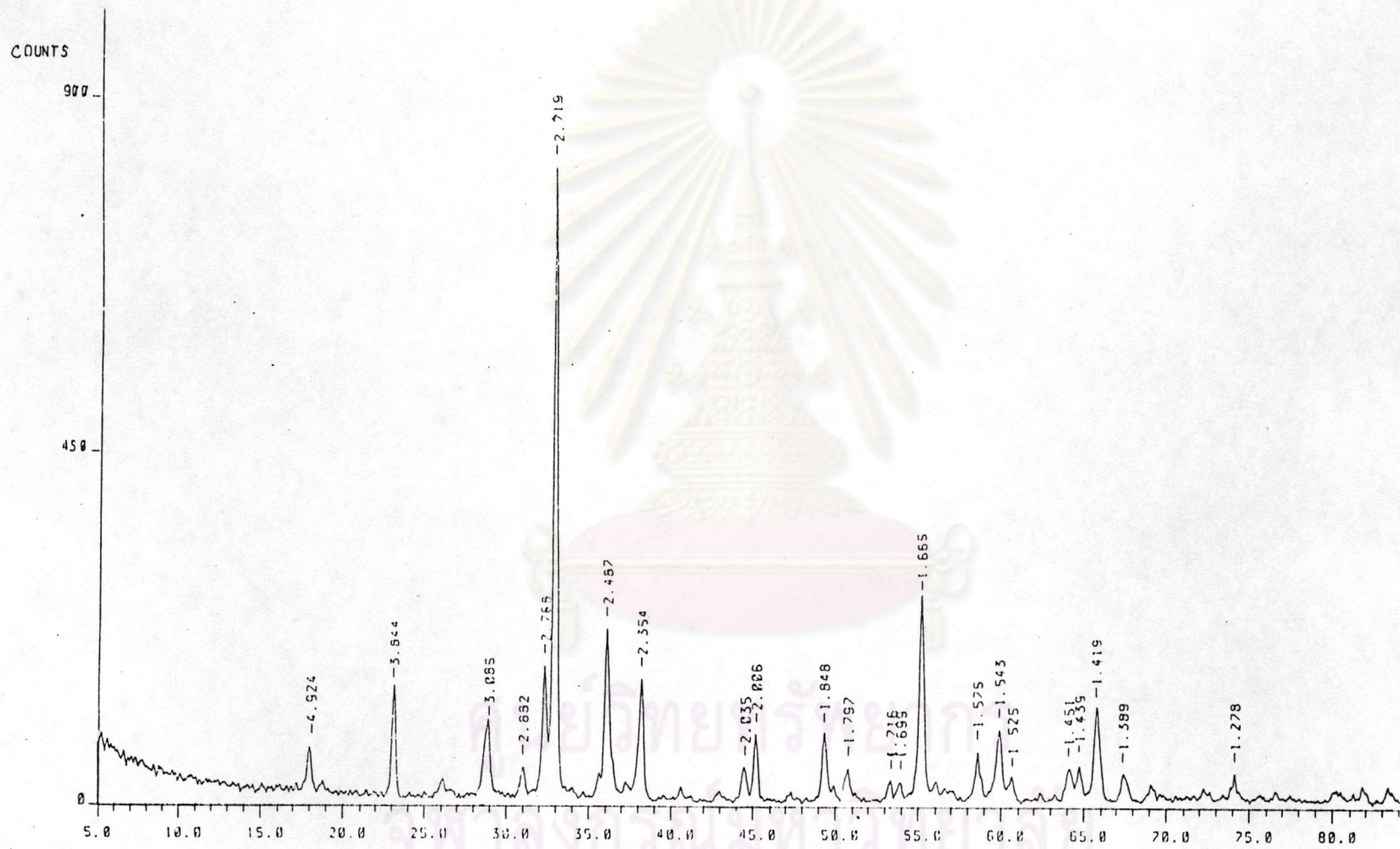


Figure 4.9 XRD pattern of the used Mn_3O_4 in the reaction of CO with O_2

Table 4.6 XRD data of the used Mn_3O_4 in the reaction of CO with O_2

D(A°)	I/I ₀
4.924	9
3.844	19
3.085	12
2.882	6
2.768	22
2.719	100
2.487	28
2.354	20
2.035	6
2.006	11
1.848	11
1.797	6
1.716	4
1.699	4
1.665	32
1.575	9
1.543	12
1.525	5
1.451	6
1.439	6
1.419	16
1.389	5
1.278	5

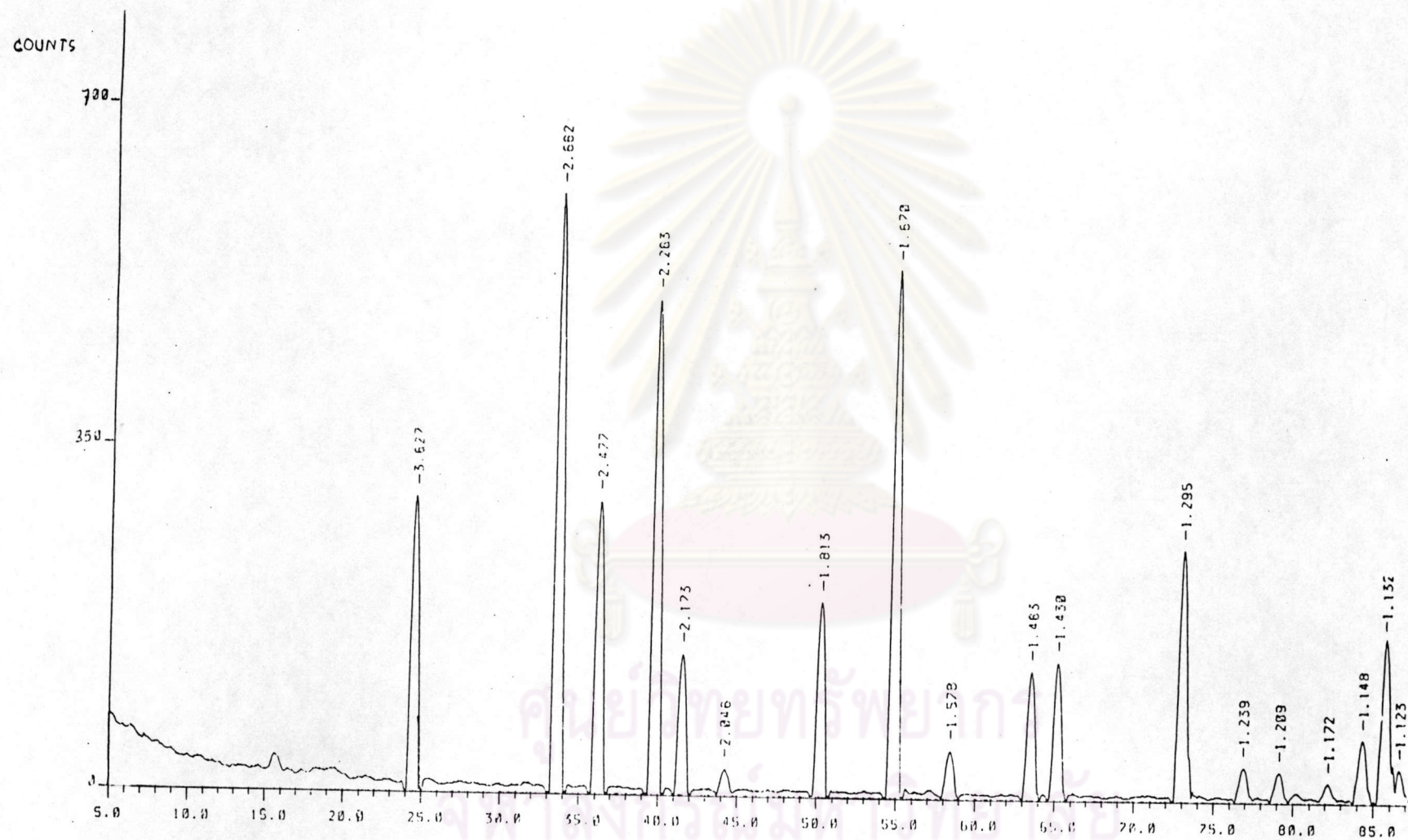


Figure 4.10 XRD pattern of the fresh Cr_2O_3

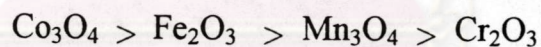
Table 4.7 XRD data of the fresh Cr₂O₃

D(A°)	I/I ₀
3.627	49
2.662	100
2.477	48
2.263	83
2.173	23
2.046	4
1.813	32
1.670	88
1.578	8
1.463	21
1.430	23
1.295	42
1.239	6
1.209	5
1.172	3
1.148	11
1.132	28
1.123	6

Comparison of the Catalytic Activity in Catalytic Oxidation Reaction

1. Comparison of the Catalytic Activity in the Reaction of CO with N₂O

The results of the catalytic oxidation reaction of CO with N₂O employing Co₃O₄, Fe₂O₃, Mn₃O₄, and Cr₂O₃ as catalysts are shown in the Figure 4.11. It was found that %CO conversion increased at the higher temperature. %CO conversion and the different metal oxide catalysts in the reaction of CO with N₂O at the temperature 200°C in Figure 4.12 shows obviously that %CO conversion of this reaction is the highest when used Co₃O₄ as a catalyst, are lower when used Fe₂O₃ and Mn₃O₄, and is the lowest when used Cr₂O₃. It is the same order (Figure 4.11) in the temperature range 180-350°C for this reaction, so the order of %CO conversion by different catalysts are as follows:



These order of % CO conversion correspond to the surface area measuring by BET method (refer to Characterization of the Catalysts by BET Method).

2. Comparison of the Catalytic Activity in the Reaction of CO with O₂

The results of the catalytic oxidation reaction of CO with O₂ employing Co₃O₄, Fe₂O₃, Mn₃O₄, and Cr₂O₃ as catalysts are shown in the

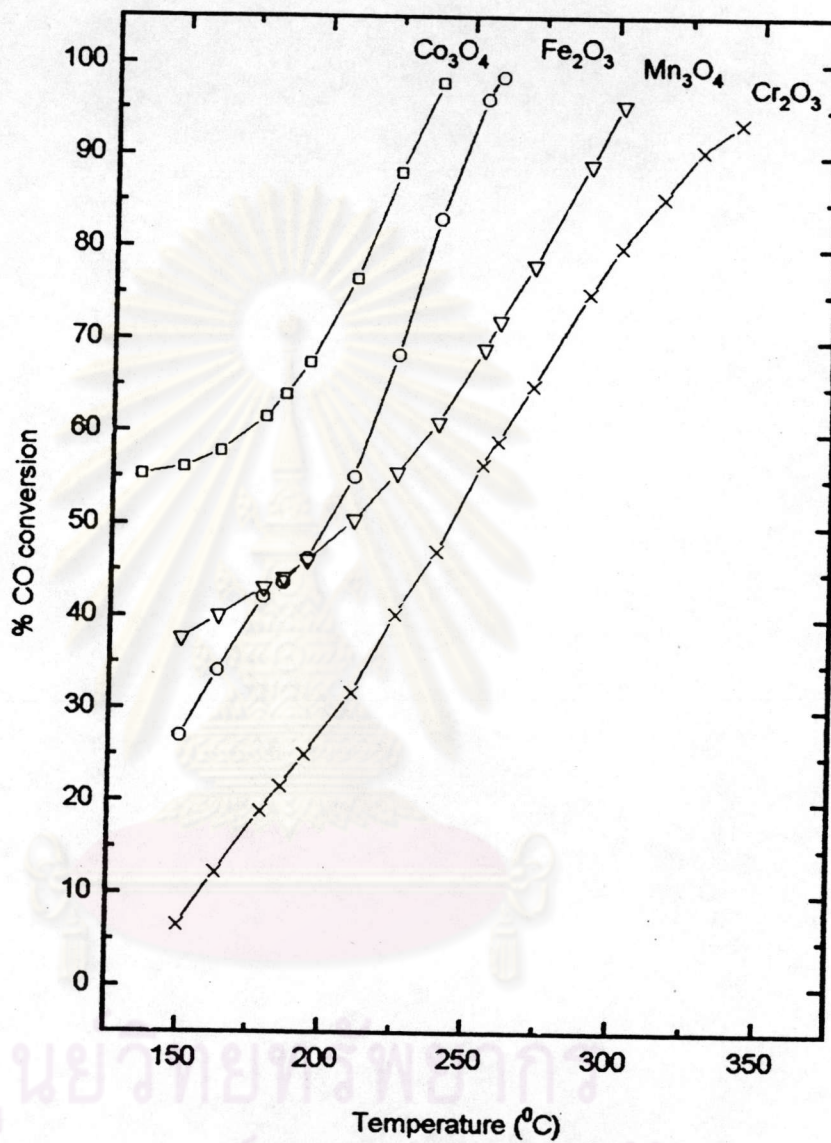


Figure 4.11 %CO conversion with temperature in the reaction of CO with N_2O by different metal oxide catalysts

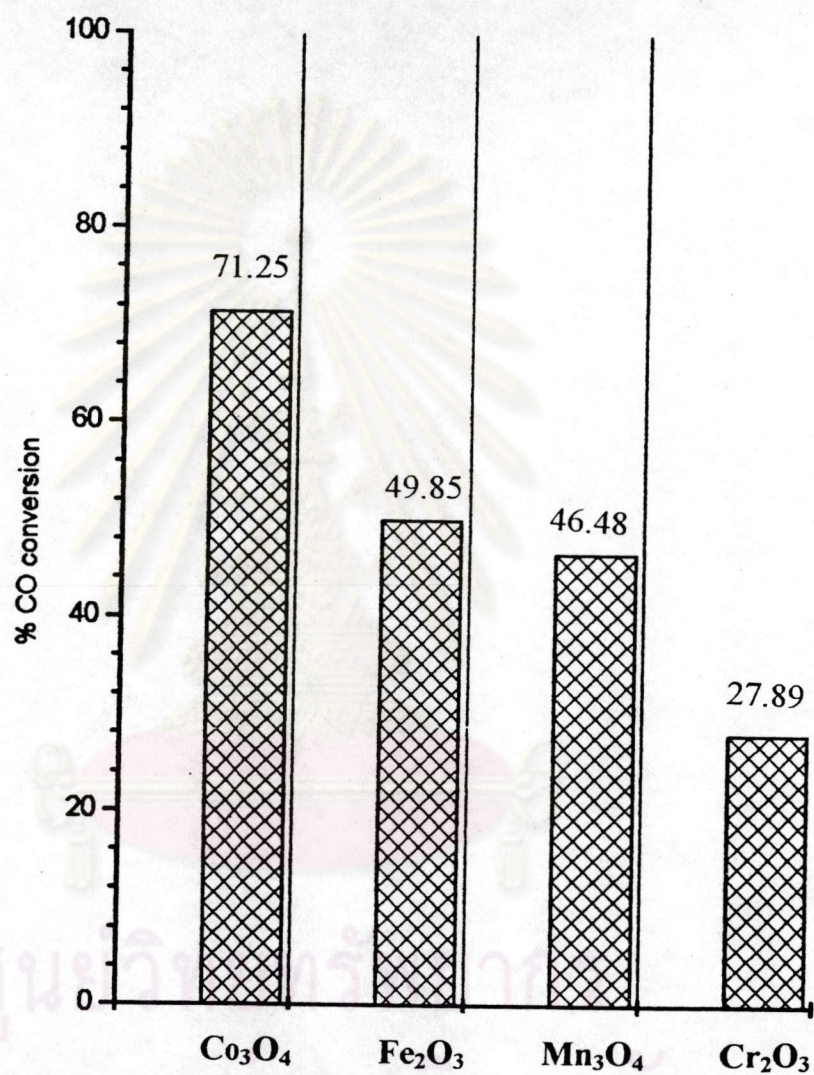
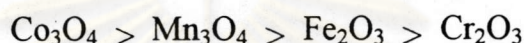
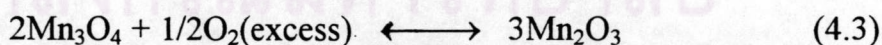


Figure 4.12 %CO conversion in the reaction of CO with N_2O by different metal oxide catalysts at 200°C

Figure 4.13. It was found that %CO conversion increased at the higher temperature. %CO conversion and different metal oxide catalysts of the reaction CO with O₂ at the temperature 200°C in Figure 4.14 shows obviously that %CO conversion of this reaction is the highest when used Co₃O₄, are lower when used Mn₃O₄ and Fe₂O₃, and the lowest when used Cr₂O₃. It is the same order (Figure 4.13) in the temperature range 130-330°C for this reaction, so the order of %CO conversion by different catalysts are as follows:



With the use of Co₃O₄, Fe₂O₃, and Cr₂O₃ as catalysts, the order of %CO conversion in the reaction of CO with O₂ is the same as those in the reaction of CO conversion in the reaction of CO with N₂O except the Mn₃O₄ catalyst that %CO conversion in the reaction of CO with N₂O (shown in Figure 4.15). The XRD pattern of the used Mn₃O₄ catalyst in the reaction of CO with O₂ (refer to Characterization of the Catalyst by XRD) showed that there was a change in the ratio of Mn₃O₄:Mn₂O₃ by the higher Mn₂O₃. Equation 4.3 (41) indicates that Mn₃O₄ has been oxidized to be Mn₂O₃ in the excess oxygen condition. The reaction of CO with O₂ that has the excess oxygen, so Mn₃O₄ could change to be Mn₂O₃ in the very amount. Mn₂O₃ is the active species catalyst in this reaction and is the more higher activity than Mn₃O₄, too.



The plot between percent peak area of CO reactant and CO₂ product against the reactor temperature (°C) in the reaction of CO with N₂O employing Co₃O₄, Fe₂O₃, Mn₃O₄, and Cr₂O₃ as catalysts are shown in Figure B.1 to B.4, respectively. The corresponding plot between percent peak area of

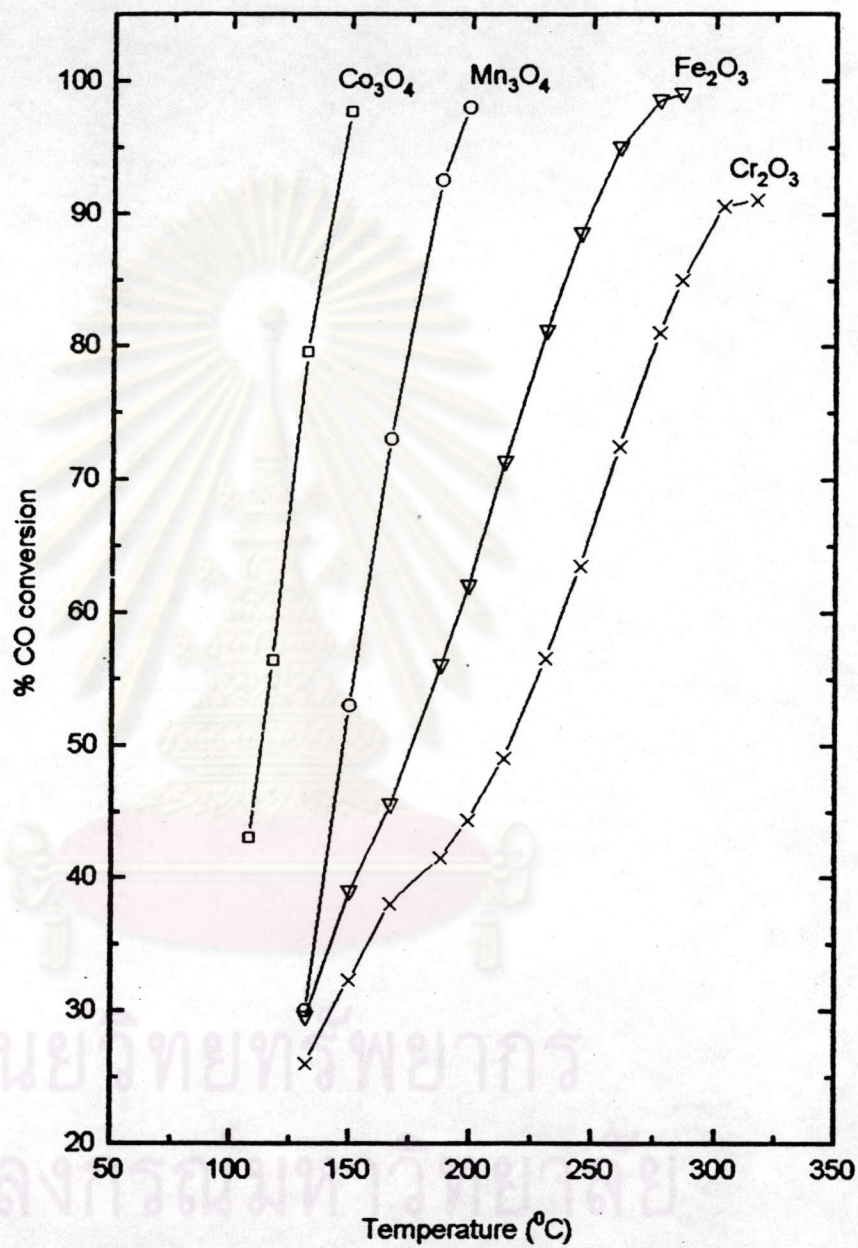


Figure 4.13 %CO conversion with temperature in the reaction of CO with O_2 by different metal oxide catalysts

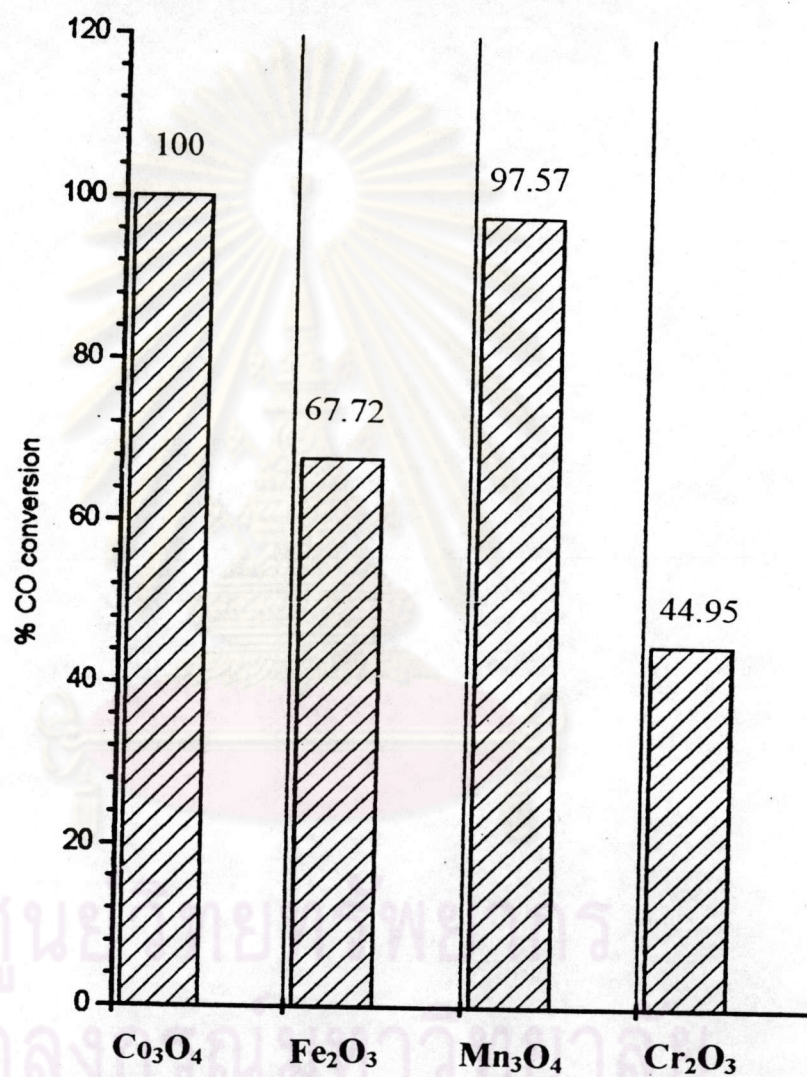


Figure 4.14 %CO conversion in the reaction of CO with O_2 by different metal oxide catalysts at 200°C

CO reactant and CO₂ product against the reactor temperature (°C) in the reaction of CO with O₂ employing Co₃O₄, Fe₂O₃, Mn₃O₄, and Cr₂O₃ as catalysts are shown in Figure B.5 to B.8, respectively.

Comparison of Catalytic Activity in the Reactions of CO with N₂O and CO with O₂

Catalytic activities termed as %CO conversion of Co₃O₄, Fe₂O₃, Mn₃O₄ and Cr₂O₃ catalysts in the reaction of CO with O₂ comparing the reaction of CO with N₂O at the temperature 200°C is shown in Figure 4.15. According to the higher percent CO conversion of all catalysts in the reaction of CO with O₂ than the reaction of CO with N₂O (it is the same result in the range of temperature 150-350°C, too), we can, therefore, conclude that oxygen is a better oxidant than nitrous oxide. This conclusion agrees with the fact that nitrous oxide is rather unreactive at low temperature (41).

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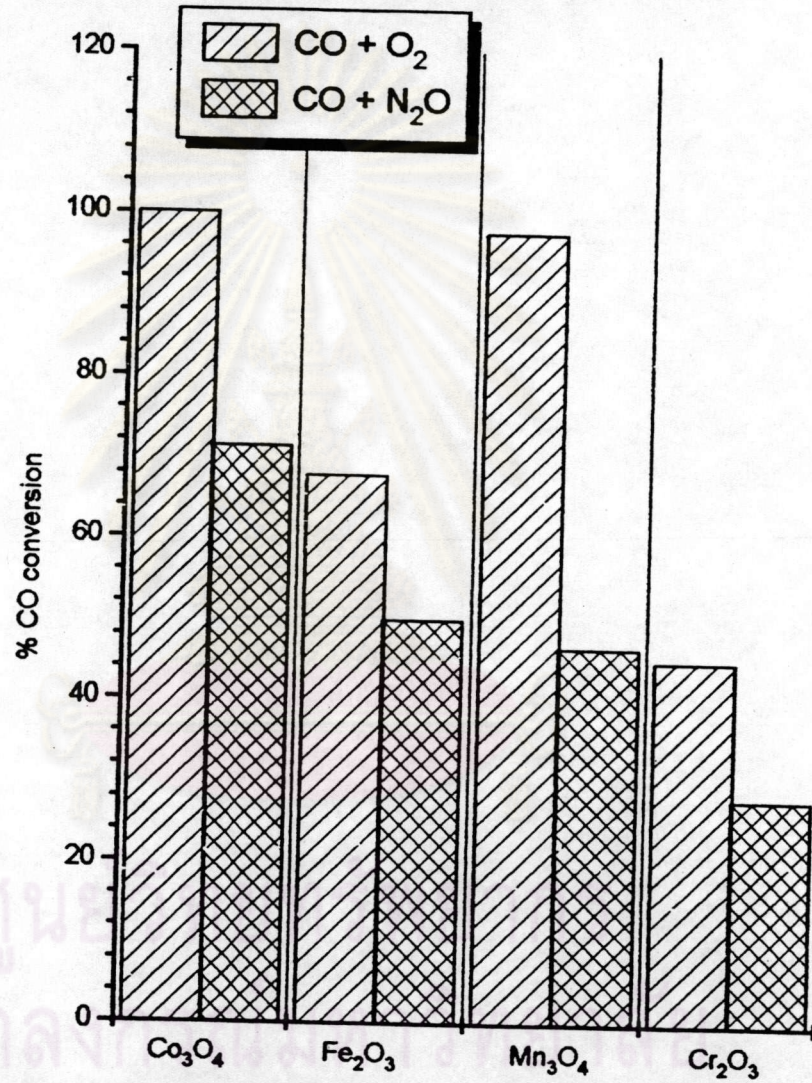


Figure 4.15 %CO conversion of the reactions and different metal oxide catalysts at the temperature 200°C