

CHAPTER V

RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two major parts including the catalyst characterization and the catalytic combustion reaction of phthalic anhydride and maleic anhydride, respectively.

5.1 Catalyst characterization

5.1.1 Determination of composition content and BET surface area of catalyst

The results of metal composition and BET surface area of all catalysts, which are analyzed by Atomic Absorption Spectroscopy (AAS) and BET surface area are summarized in Tables 5.1 and 5.2.

Table 5.1 The composition of different magnesium loading catalyst and BET surface area

Catalyst	%Co content	%Mg content	BET surface area (m ² /g)
Co ₃ O ₄ /Al ₂ O ₃	8.9	-	178
8Co0.5MgO/Al ₂ O ₃	8.0	0.46	218
8Co1MgO/Al ₂ O ₃	8.1	0.68	124
8Co2MgO/Al ₂ O ₃	8.0	1.5	166
8Co3MgO/Al ₂ O ₃	7.6	3.3	195

Table 5.2 The composition of different cobalt loading catalyst and BET surface area

Catalyst	%Co content	%Mg content	BET surface area (m ² /g)
MgO/Al ₂ O ₃	-	1.1	244
6Co1MgO/Al ₂ O ₃	6.2	0.80	197
7Co1MgO/Al ₂ O ₃	6.9	0.96	187
8Co1MgO/Al ₂ O ₃	8.1	0.68	124
9Co1MgO/Al ₂ O ₃	8.8	1.4	230
10Co1MgO/Al ₂ O ₃	9.8	0.84	193

The data in Tables 5.1 and 5.2 indicate that the cobalt and magnesium contents in Co-Mg-O/Al₂O₃ sample are close to calculated value and could not define the correlation between the cobalt and magnesium amounts and the surface area.

5.1.2 Fourier Transform Infrared Spectrometer (FT-IR)

The IR spectrum is used to identify the functional group on the surface of catalyst. The infrared radiation is used in the wavelength of 400-2000 cm⁻¹.

The IR spectra of Co-Mg-O/Al₂O₃ catalysts are showed in Figures 5.1 - 5.2. Figure 5.1 shows the IR spectra of different Mg loading catalysts. Figure 5.2 shows the IR spectra of different Co loading catalysts. The IR absorption bands are measured in the region 400-900 cm⁻¹ exhibit the same IR spectrum as detected on JRC ALO2. From literature, the IR absorption bands of cobalt oxide occur at 385, 580, and 667 cm⁻¹ [Busca *et al* (1990)]. This means that cobalt oxide appears in the forms of crystalline Co₃O₄ on the Al₂O₃ surface for all Co-Mg-O/Al₂O₃ system and the absorption frequency of cobalt oxide in Co-Mg-O/Al₂O₃ catalyst is not measurable because in these regions the IR spectra of cobalt oxide may be hidden by the absorption of Al₂O₃.

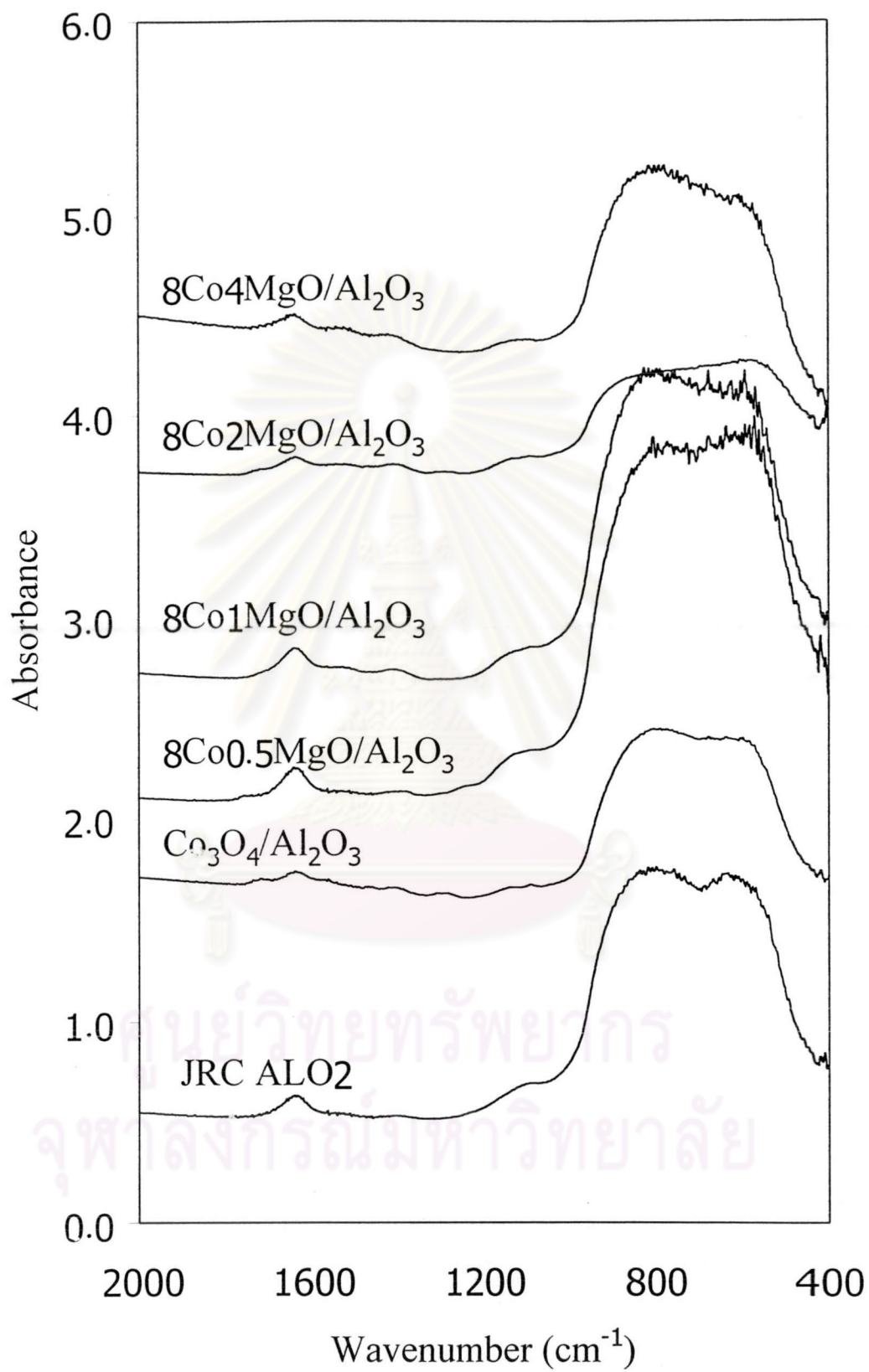


Figure 5.1 IR spectra of different magnesium loading catalysts

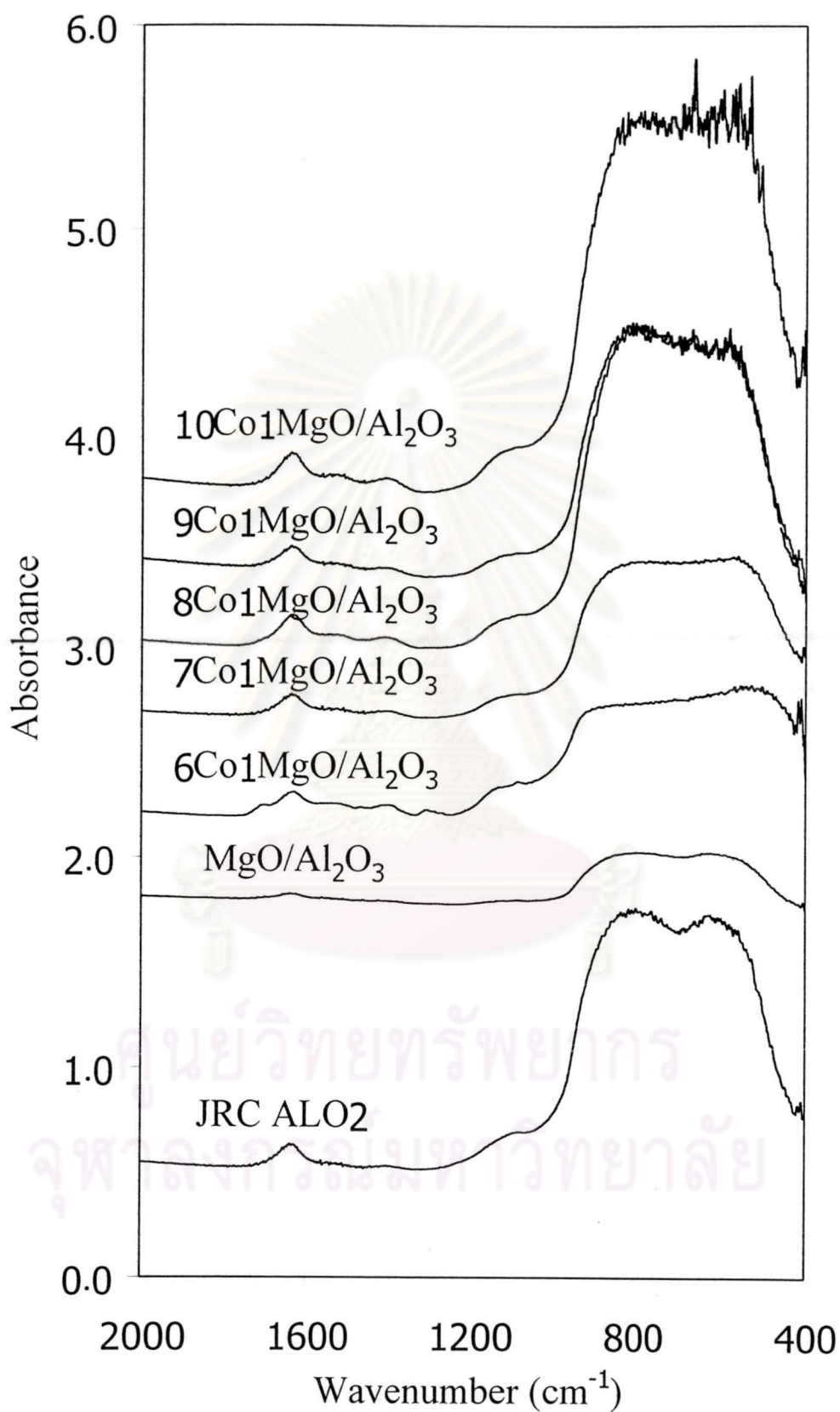


Figure 5.2 IR spectra of different cobalt loading catalysts

5.1.3 X-ray Diffraction (XRD)

The crystal structure of catalysts is identified by X-ray Diffraction technique. Figures 5.3-5.4 reveal the results of XRD spectra of different magnesium and cobalt loading of Co-Mg-O/Al₂O₃ catalysts.

From a previous research, the XRD pattern of Co₃O₄ catalyst shows 6 peaks at 20°, 32°, 37°, 45°, 60° and 65.5° [Petryle and co-workers (2000)]. The XRD patterns of Co-Mg-O/Al₂O₃ catalysts in Figures 5.3 and 5.4 are the same as Al₂O₃ support. The XRD pattern of Al₂O₃ catalyst shows 4 peaks at 37°, 45°, 46°, and 65.5° that are the same position as Co₃O₄ catalyst. This means that the crystalline Co₃O₄ catalyst peaks in Co-Mg-O/Al₂O₃ catalyst are not measurable because in these regions sine the XRD patterns of Co₃O₄ are hidden by the XRD patterns of Al₂O₃ support.



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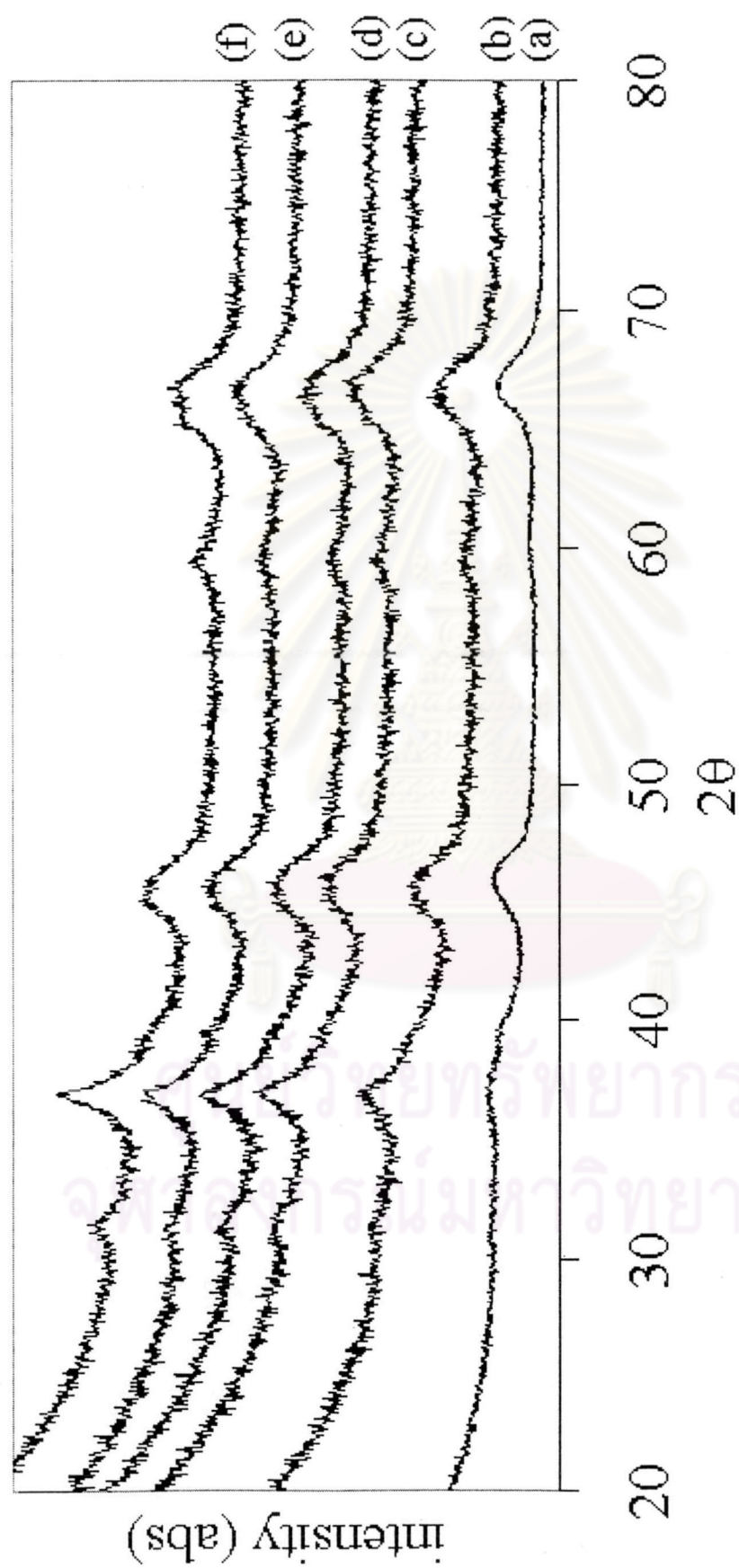


Figure 5.3 The XRD pattern of different magnesium loading catalysts

(a) JRC AlO_2 , (b) $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$, (c) $8\text{Co}0.5\text{MgO}/\text{Al}_2\text{O}_3$, (d) $8\text{Co}1\text{MgO}/\text{Al}_2\text{O}_3$, (e) $8\text{Co}2\text{MgO}/\text{Al}_2\text{O}_3$, (f) $8\text{Co}3\text{MgO}/\text{Al}_2\text{O}_3$

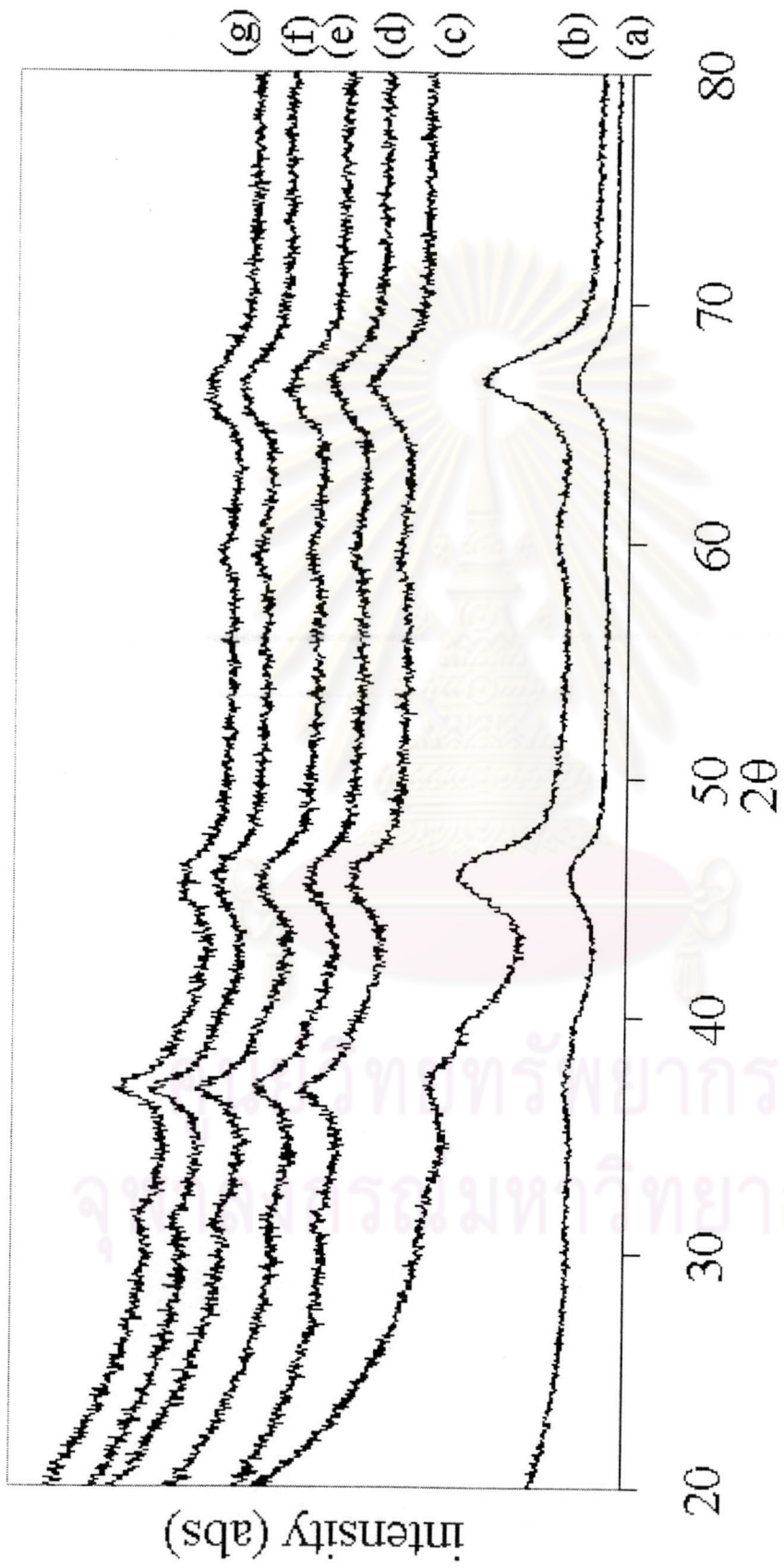


Figure 5.4 The XRD pattern of different cobalt loading catalysts

(a) JRC Al_2O_3 , (b) $\text{MgO}/\text{Al}_2\text{O}_3$, (c) $6\text{Co}/\text{MgO}/\text{Al}_2\text{O}_3$, (d) $7\text{Co}/\text{MgO}/\text{Al}_2\text{O}_3$, (e) $8\text{Co}/\text{MgO}/\text{Al}_2\text{O}_3$, (f) $9\text{Co}/\text{MgO}/\text{Al}_2\text{O}_3$, (g) $10\text{Co}/\text{MgO}/\text{Al}_2\text{O}_3$.

5.2 Catalytic reaction

In this work, the role of magnesium in the Co-Mg-O/Al₂O₃ catalyst and the effect of different cobalt and magnesium contents in the Co-Mg-O/Al₂O₃ catalyst are received much attention. Since the Co-Mg-O/Al₂O₃ system is a novel system that have no information about its catalytic property. Therefore, the oxidation properties of Co-Mg-O/Al₂O₃ catalysts are studied by using the combustion reaction on phthalic anhydride and maleic anhydride as test reaction.

5.2.1 Effect of magnesium loading

- *phthalic anhydride combustion*

Figure 5.5 shows the catalytic activity of Al₂O₃, Co₃O₄/Al₂O₃, MgO/Al₂O₃, and Co-Mg-O/Al₂O₃ catalysts for phthalic anhydride combustion. For Co-Mg-O/Al₂O₃ catalyst, the conversion of phthalic anhydride increased from 30 to 85% at the temperature range of 200 to 300°C and steadily increased until the temperature reached 550°C, which the conversion was about 91%. On the other hand, Al₂O₃ catalyst, phthalic anhydride conversion enhanced from 5 to 80%. The conversion steadily increased from 5 to 80% at the temperature range of 200 to 550°C for MgO/Al₂O₃ catalyst, while Co₃O₄/Al₂O₃ catalyst showed the conversion close to the conversion of Al₂O₃ catalyst with higher conversions. The reaction products observed CO₂ and H₂O. No CO appeared in the effluent gas.

MgO/Al₂O₃ catalyst shows the phthalic anhydride conversion lower than Al₂O₃ support, indicating that magnesium was not able to catalyze the reaction. Moreover it inhibited the ability to catalyze the reaction of Al₂O₃. The result is MgO blocking the active site of Al₂O₃. On the other hand, Co₃O₄/Al₂O₃ showed the higher conversion than Al₂O₃ catalyst. When loading magnesium into catalyst, Co-Mg-O/Al₂O₃ increased the phthalic anhydride conversion. The conversion was increased about 55% at the temperature range of 200 to 300°C, indicated that magnesium is able to improved the catalytic activity of Co₃O₄/Al₂O₃ catalyst. The result reveals that loading magnesium into Co₃O₄/Al₂O₃ catalyst to form a Co-Mg-O/Al₂O₃ catalyst

gives higher conversion about 20%. This prove that the role of magnesium in Co-Mg-O/Al₂O₃ catalyst is promoter.

- *maleic anhydride combustion*

The catalytic activities of Al₂O₃, Co₃O₄/Al₂O₃, MgO/Al₂O₃, and Co-Mg-O/Al₂O₃ for the combustion of maleic anhydride are exhibited in Figure 5.6. The conversion of maleic anhydride on Al₂O₃, Co₃O₄/Al₂O₃, MgO/Al₂O₃, and CoMgO/Al₂O₃ increased in the temperature range of 200 to 550°C for 2 to 90%, 5 to 93%, 3 to 85%, and 12 to 98%, respectively. The reaction products observed CO₂ and H₂O. No CO appeared in the effluent gas.

Compared the phthalic anhydride combustion and the maleic anhydride combustion, it is found that magnesium shows the role of promoter for both anhydride combustions. Magnesium oxide promoted the adsorption of anhydride on the catalyst surface, thus, provides more opportunity for the anhydride to react with cobalt. The maleic anhydride conversion was higher than phthalic anhydride conversion because maleic anhydride's structure was easier to decompose than phthalic anhydride's structure. The phthalic anhydride has the active position to initiate the reaction only at the anhydride ring while the benzene ring is hardly to decompose. The test to find the initiate reaction position was investigated by using the combustion reaction of benzene and alkyl benzenes such as toluene and ethylbenzene. From Figures 5.7-5.9 it was found that the conversion of benzene reaches 100% at 550°C while 100% toluene conversion is achieved at about 450°C and 100% ethylbenzene conversion is achieved at about 350°C. The reaction products observed are only CO₂ and H₂O.

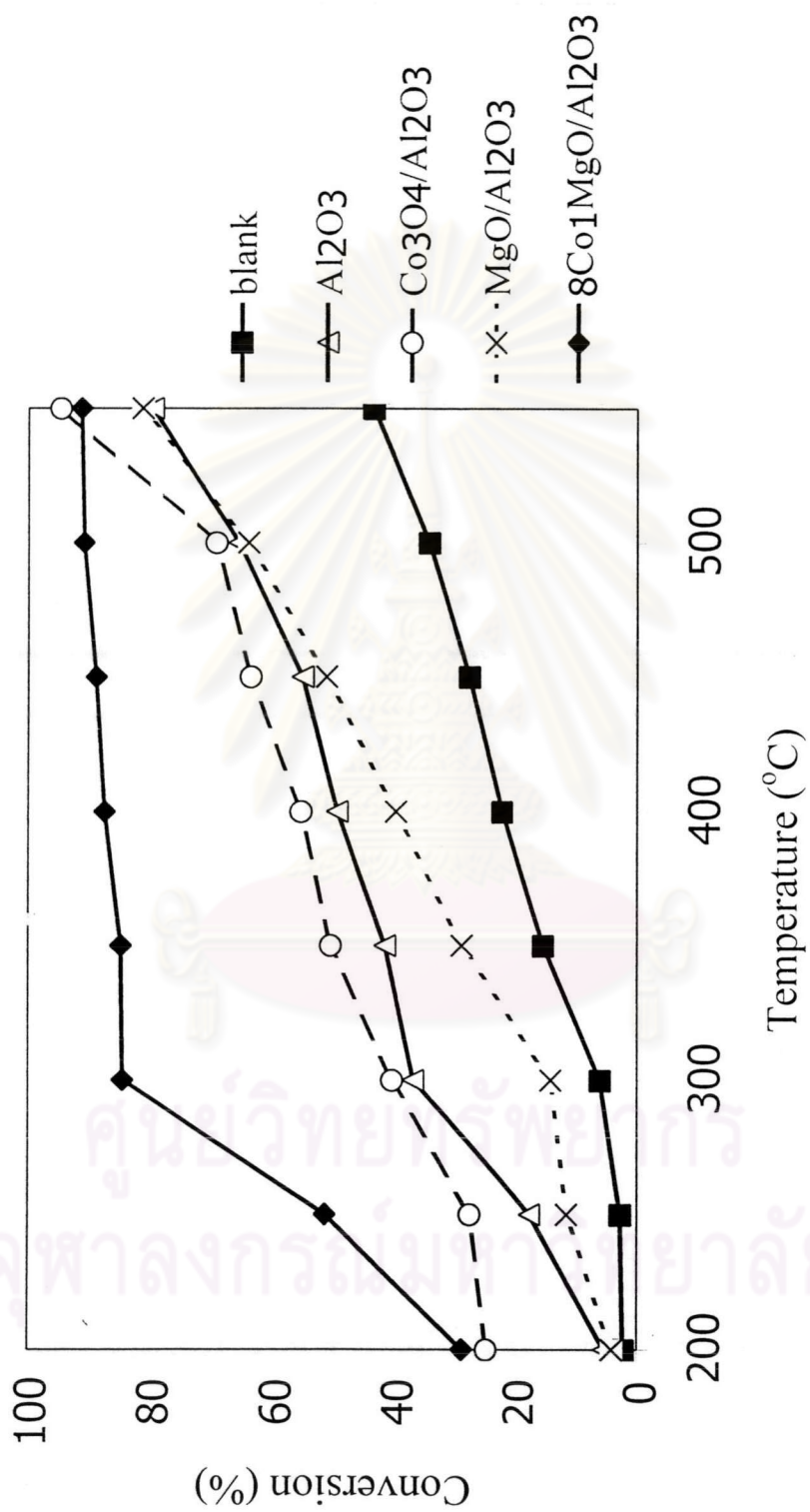


Figure 5.5 Catalytic activity of Al₂O₃, Co₃O₄/Al₂O₃, MgO/Al₂O₃, and 8Co1MgO/Al₂O₃ catalyst for phthalic anhydride combustion with feed contains 0.05 mol% phthalic anhydride in air

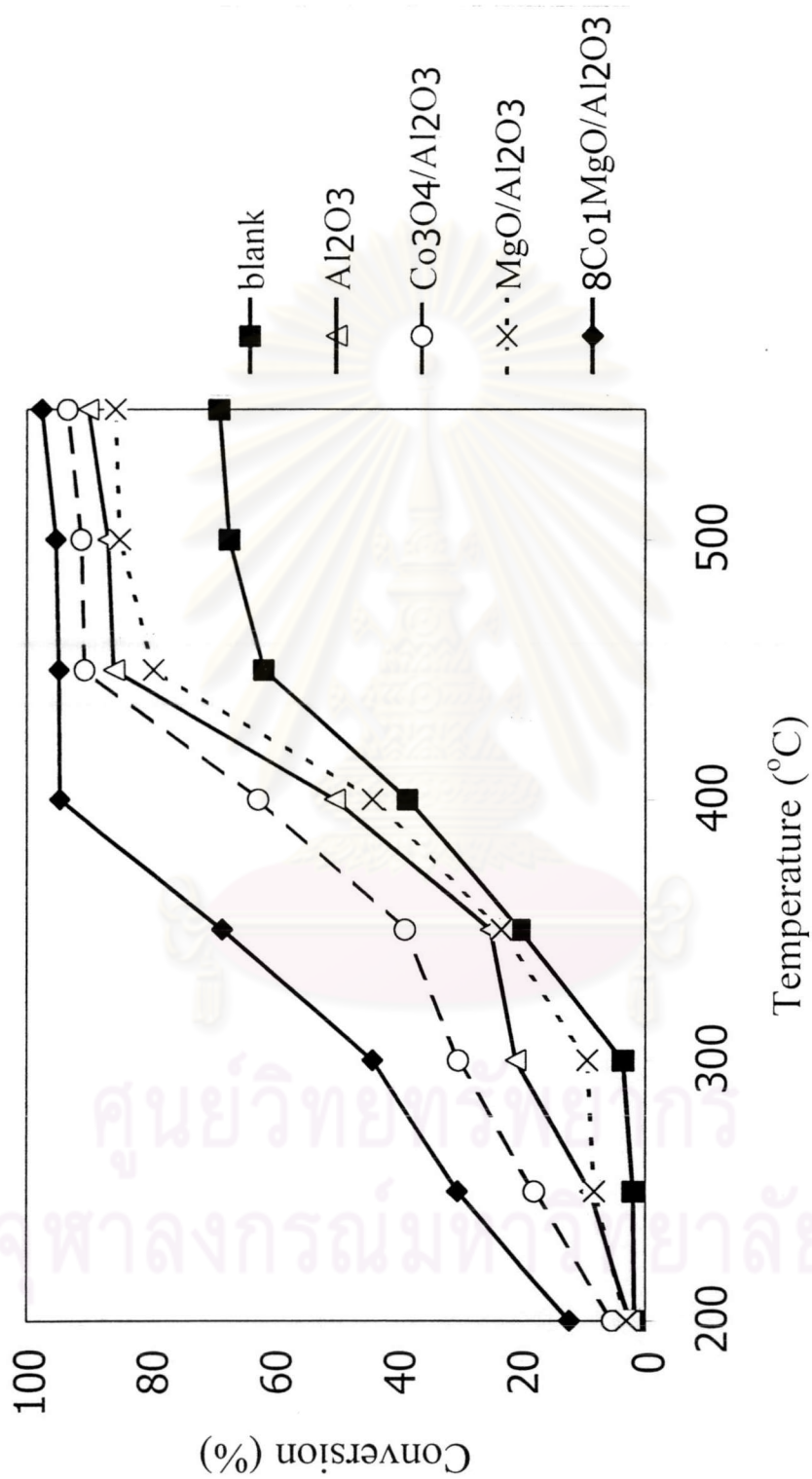


Figure 5.6 Catalytic activity of Al₂O₃, Co₃O₄/Al₂O₃, MgO/Al₂O₃, and 8Co1MgO/Al₂O₃ catalyst for maleic anhydride combustion with feed contains 0.05 mol% maleic anhydride in air

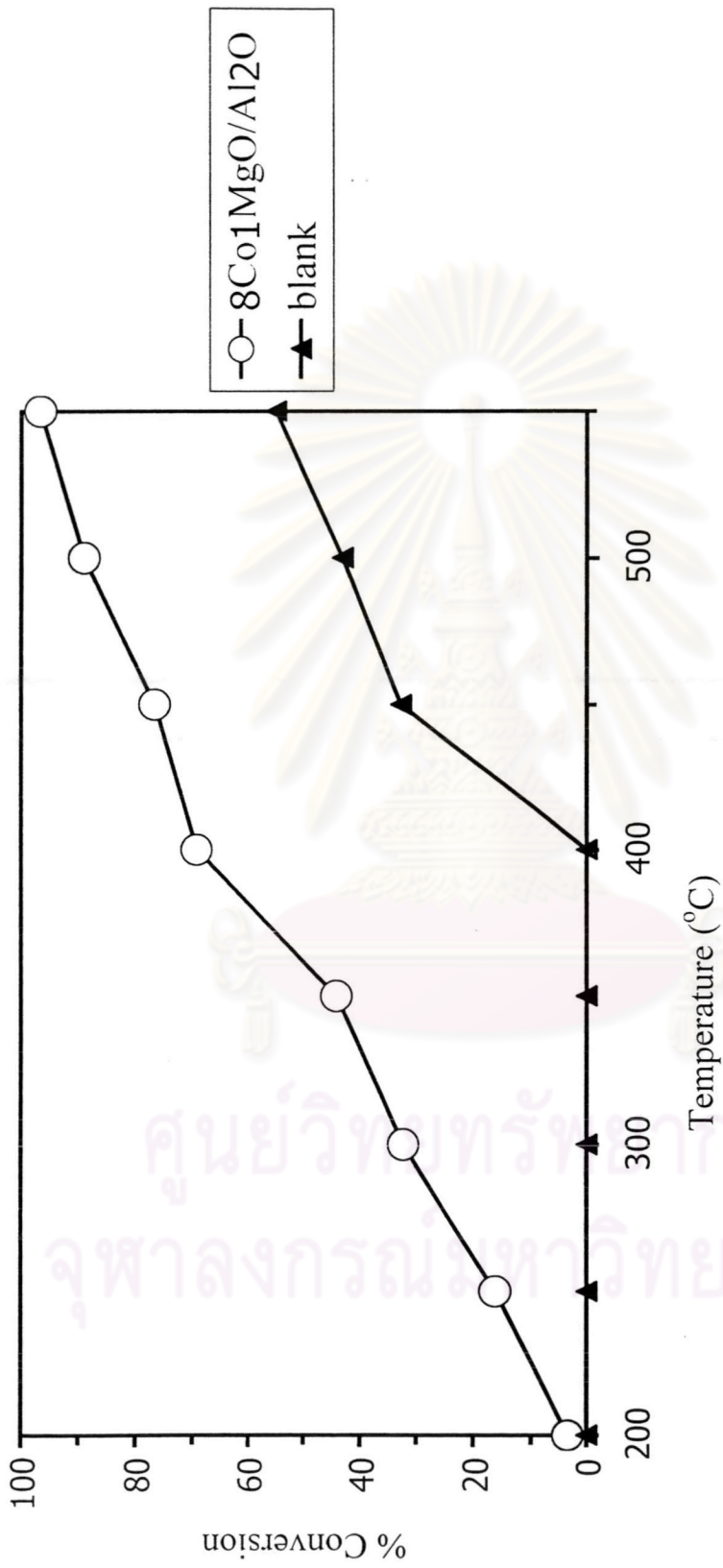


Figure 5.7 The catalytic activity of 8Co1MgO/Al₂O₃ catalyst for benzene combustion with feed contains 0.03 mol% benzene in air

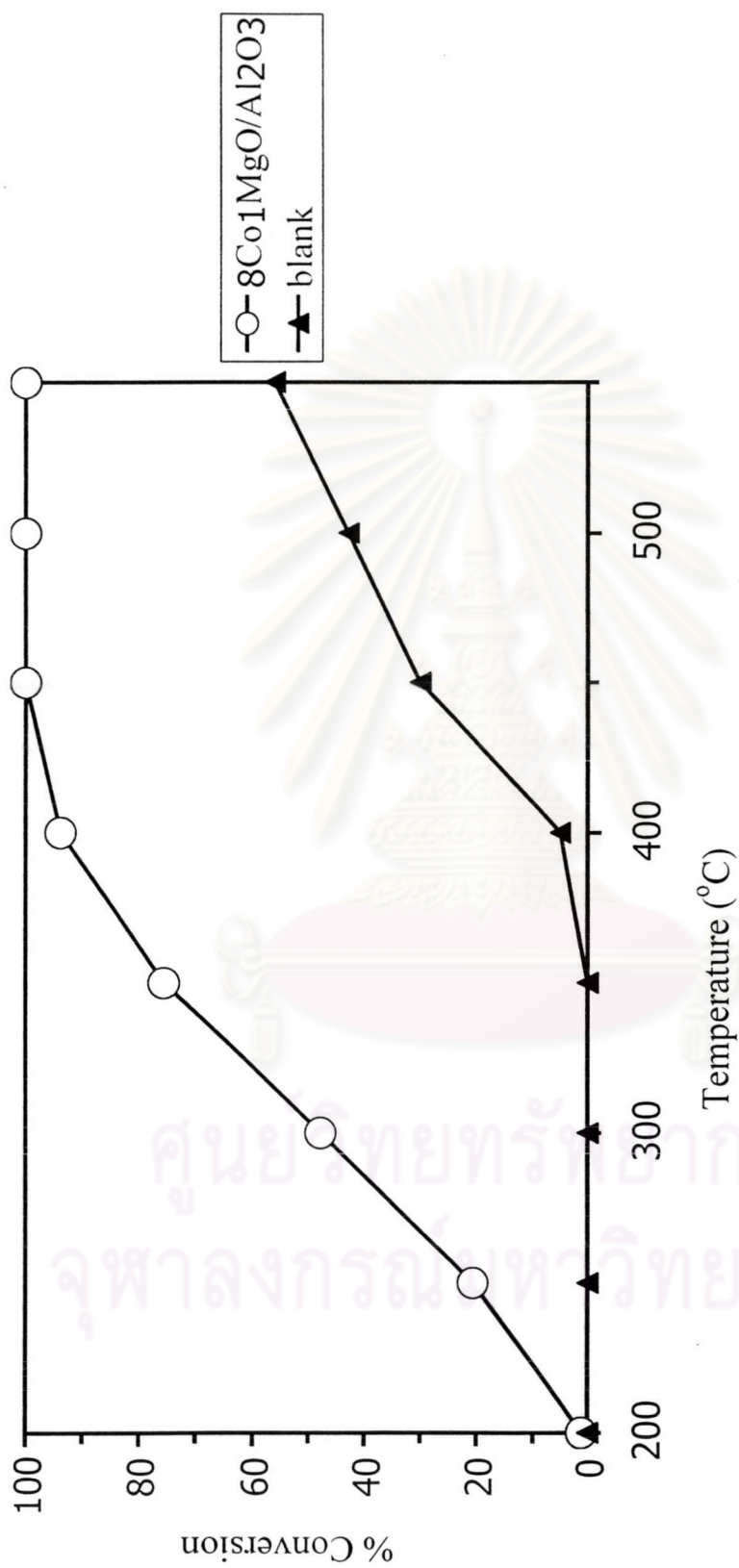


Figure 5.8 The catalytic activity of 8Co1MgO/Al₂O₃ catalyst for toluene combustion with feed contains 0.03 mol% toluene in air

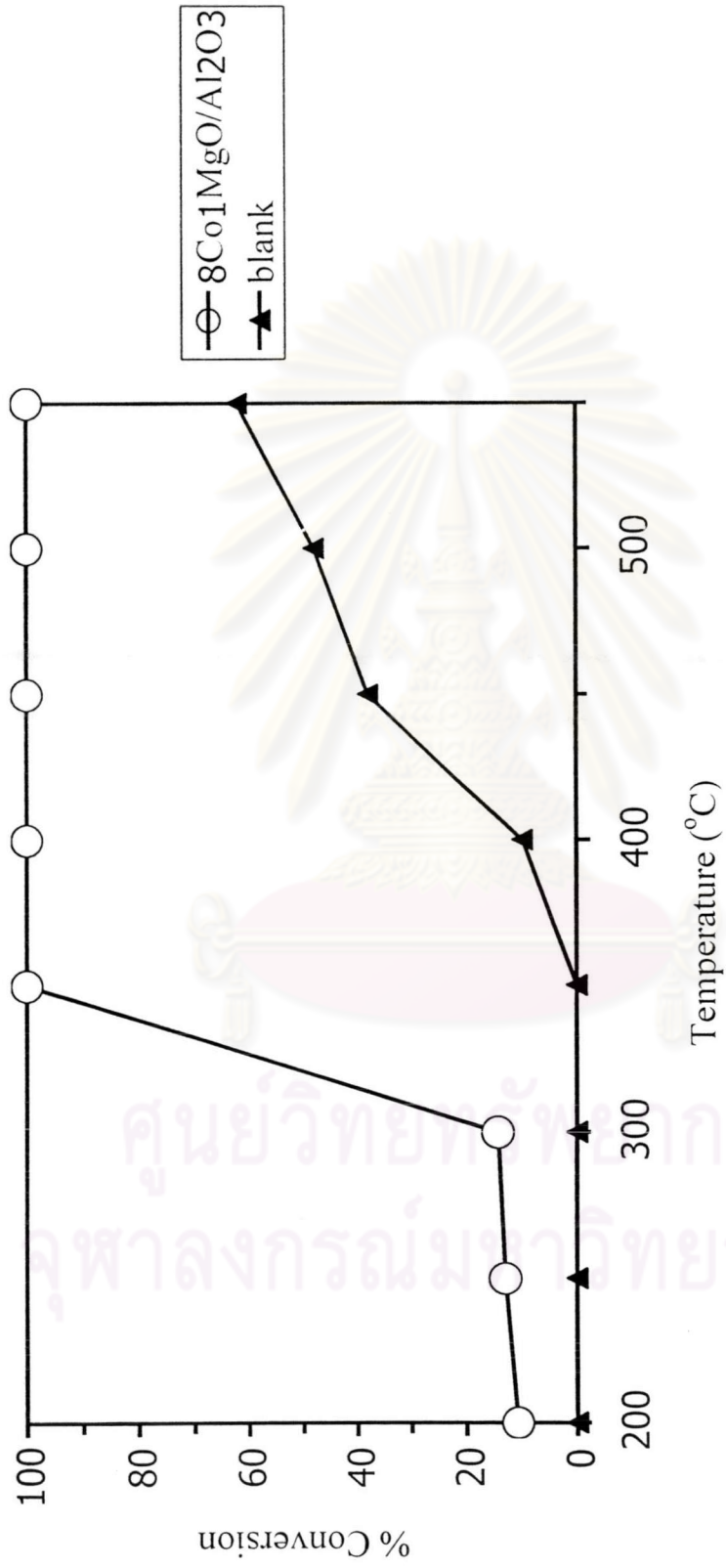


Figure 5.9 The catalytic activity of 8Co1MgO/Al₂O₃ catalyst for ethylbenzene combustion with feed contains 0.03 mol% ethylbenzene in air

Theoretically the oxidation at the methyl group attaches to the benzene ring of toluene is easier than the direct attack at the aromatic ring. The results of toluene oxidation exhibited in Figure 5.8 also show that toluene is easier to be oxidized than benzene. The existing of the methylene group (CH_2) of the ethyl group attaches to the benzene ring allows ethylbenzene to be more active than toluene in the oxidation process. The results exhibited in Figure 5.9 confirm the above hypothesis. These results indicate that alkyl aromatic is easier to be decomposed than aromatic ring. Therefore the position of reaction initiation is not likely to be the benzene ring. The test of the combustion reaction of acetic acid in Figure 5.10 showed that acetic acid was rapidly decomposed that may be due to the rather small molecule of acetic acid.

The oxidation of phthalic anhydride will occur only when phthalic anhydride approaches the catalyst surface with the anhydride group points to the surface. (see Figure 5.11a) Then, the adsorption of phthalic anhydride can occur, leading to the combustion of phthalic anhydride molecule. If the phthalic anhydride molecule approaches the catalyst surface with its benzene ring points to the surface, the adsorption of the phthalic anhydride molecule is not likely to be occurred. Therefore, no phthalic anhydride combustion occurs.

The oxidation of maleic anhydride is similar to that of phthalic anhydride but is rather easier. The oxidation can occurs independently from the structure of maleic anhydride molecule points to the catalyst surface (the anhydride group or the $\text{C}=\text{C}$ bond) as shown in Figure 5.11b.

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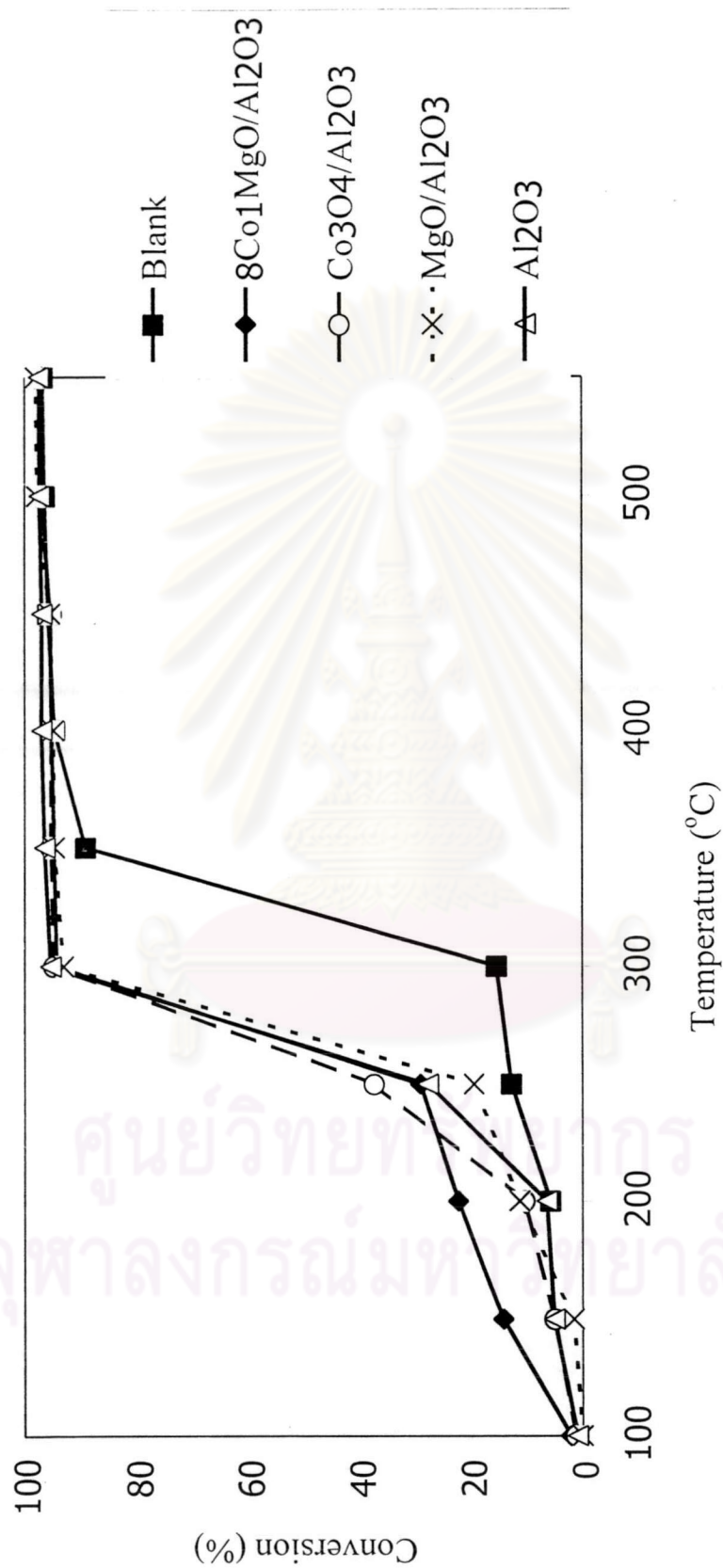


Figure 5.10 Catalytic activity of Al₂O₃, Co₃O₄/Al₂O₃, MgO/Al₂O₃, and 8Co1MgO/Al₂O₃ catalyst for acetic acid combustion with feed contains 0.03 mol% acetic acid in air

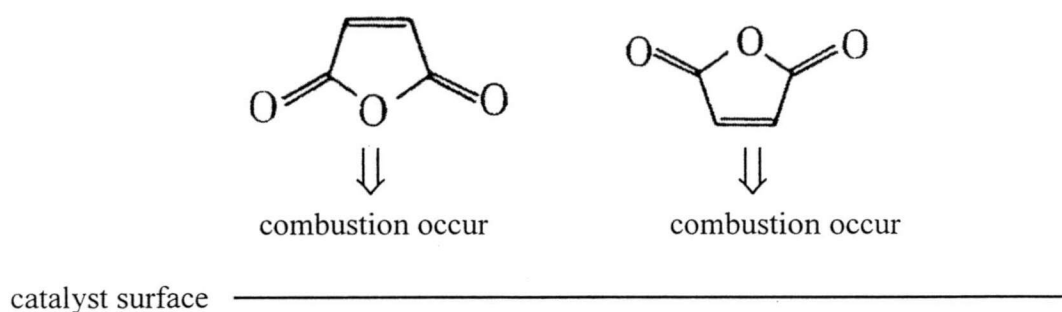


Figure 5.11a The maleic anhydride approaches the catalyst surface

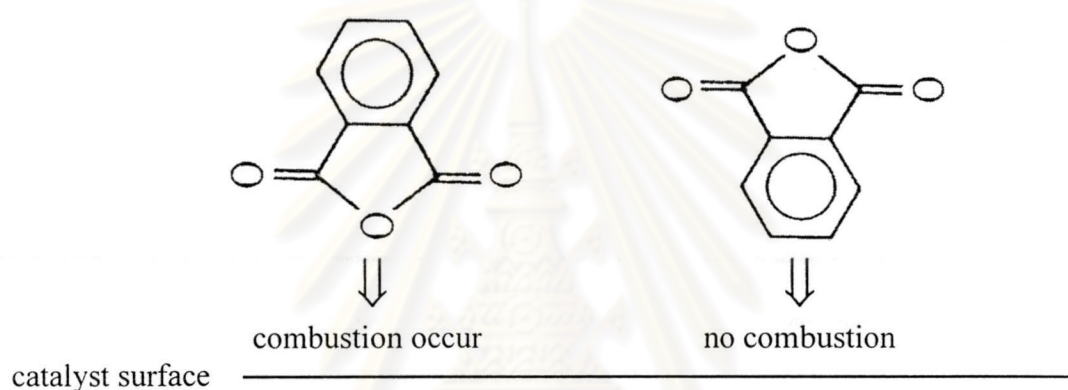


Figure 5.11b The phthalic anhydride approaches the catalyst surface

5.2.2 The optimum ratio of Co:Mg on catalyst

- *fixed Co wt% with various Mg wt%*
- *phthalic anhydride combustion*

Figure 5.12 shows the phthalic anhydride conversions over Co-Mg-O/Al₂O₃ catalysts that the amount of Co is fixed at around 8 wt%, while the amount of magnesium is varied to find the optimum amount of magnesium. It is found that 8Co1MgO/Al₂O₃ shows the best conversion, which increased from 30 to 85% in the range of temperature at 200 to 300°C and steadily raised until the temperature reached 550°C, which the conversion was about 91%. While 8Co3MgO/Al₂O₃, 8Co2MgO/Al₂O₃, and 8Co0.5MgO/Al₂O₃ exhibit almost the same conversion as about 15 to 90 % in the range of temperature at 200 to 550°C. The catalytic activity

of these catalysts is in the order of $8\text{Co}1\text{MgO}/\text{Al}_2\text{O}_3 > 8\text{Co}3\text{MgO}/\text{Al}_2\text{O}_3 > 8\text{Co}2\text{MgO}/\text{Al}_2\text{O}_3 > 8\text{Co}0.5\text{MgO}/\text{Al}_2\text{O}_3$.

- *Maleic anhydride combustion*

The catalytic activity of Co-Mg-O/ Al_2O_3 catalysts that the amount of cobalt is fixed at 8 wt%, while the amount of magnesium is varied to find the optimum amount of magnesium, is shown in Figure 5.13. The $8\text{Co}1\text{MgO}/\text{Al}_2\text{O}_3$ catalyst shows the best conversion, which enhanced from 12 to 98% with reaction temperature from 200 to 550°C. While $8\text{Co}3\text{MgO}/\text{Al}_2\text{O}_3$, $8\text{Co}2\text{MgO}/\text{Al}_2\text{O}_3$, and $8\text{Co}0.5\text{MgO}/\text{Al}_2\text{O}_3$ showed the conversion about 5 to 90 % in the range of temperature at 200 to 550°C. The catalytic activity of the catalyst decreased in the order of $8\text{Co}1\text{MgO}/\text{Al}_2\text{O}_3 > 8\text{Co}2\text{MgO}/\text{Al}_2\text{O}_3 > 8\text{Co}0.5\text{MgO}/\text{Al}_2\text{O}_3 > 8\text{Co}3\text{MgO}/\text{Al}_2\text{O}_3$.

From both catalytic combustions, the optimum amount of magnesium was around 1 wt%. The different magnesium loading affected the catalytic activity of Co-Mg-O/ Al_2O_3 catalyst that may be because magnesium inhibits the catalytic activity of alumina activity. In contrast, magnesium oxide promotes the adsorption of anhydride on the catalyst surface, thus, provide more opportunity to react with cobalt, resulting in higher activity. The amount of magnesium loading related to inhibition of alumina activity and ability of acid to stay on the catalyst surface.

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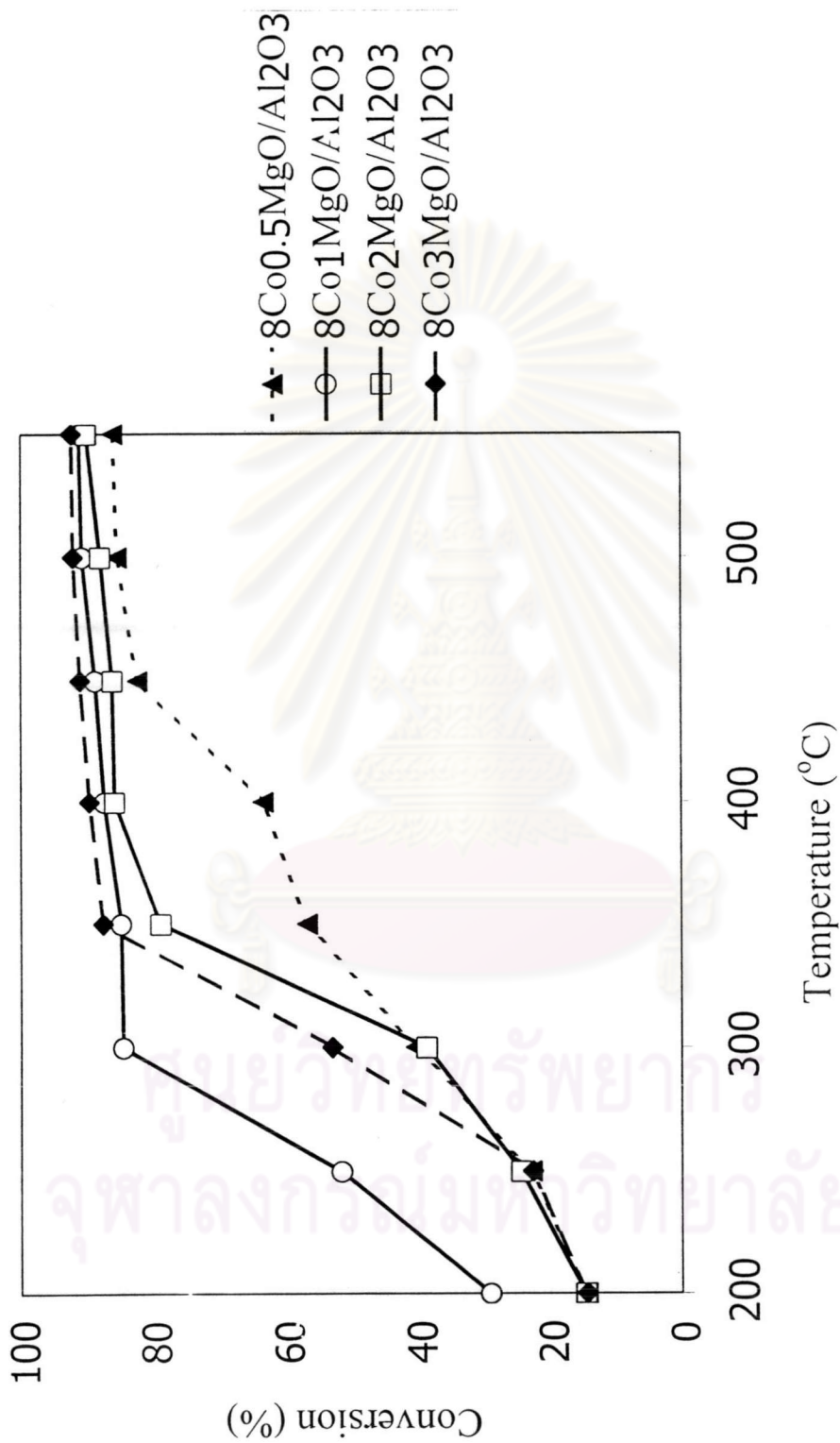


Figure 5.12 Catalytic activity of Co-Mg-O/Al₂O₃ catalysts that fixed Co at 8wt% with various Mg wt% for phthalic anhydride combustion with feed contains 0.05 mol% phthalic anhydride in air

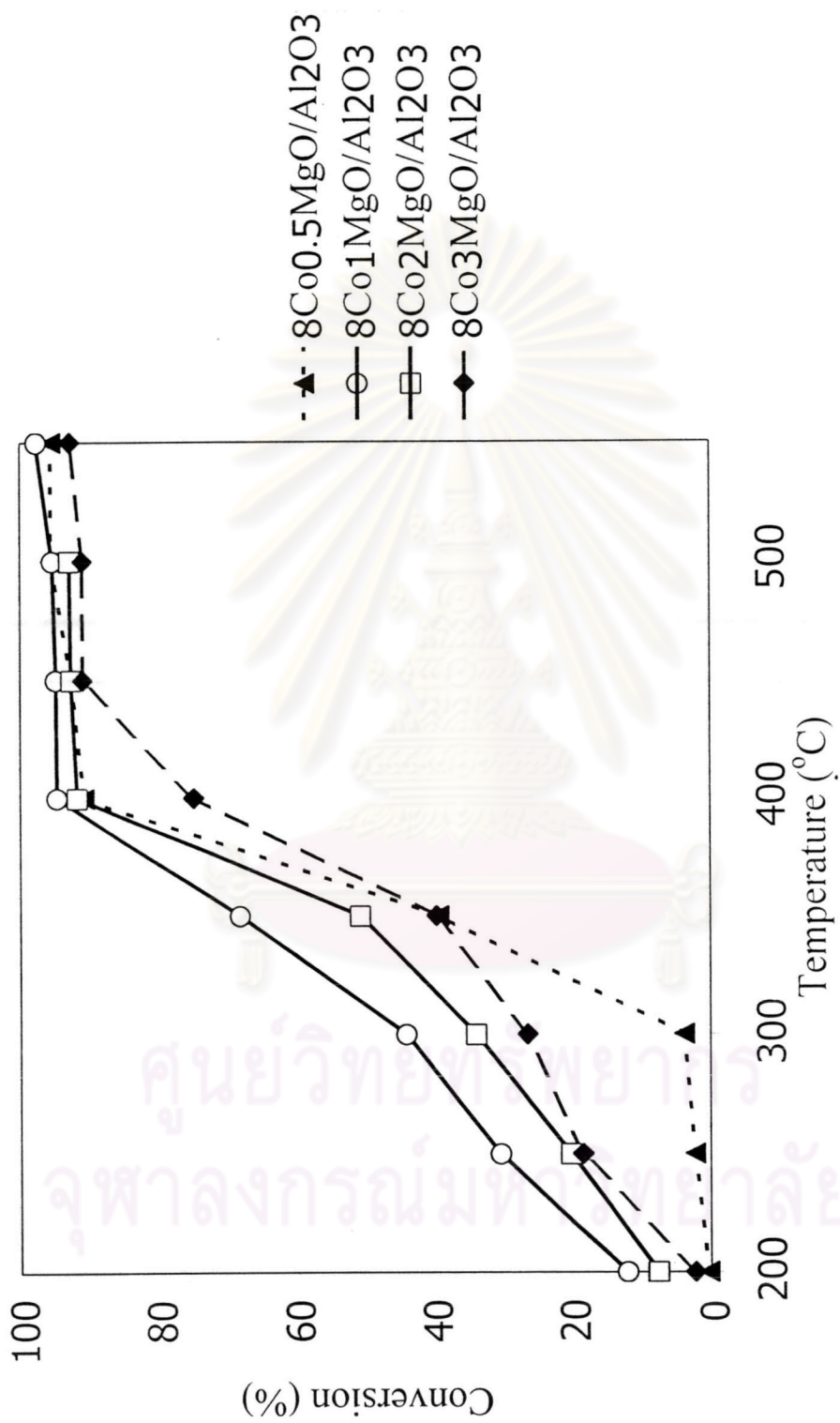


Figure 5.13 Catalytic activity of Co-Mg-O/Al₂O₃ catalysts that fixed Co at 8wt% with various Mg wt% for maleic anhydride combustion with feed contains 0.05 mol% maleic anhydride in air

- *fixed Mg wt% with various Co wt%*

- *phthalic anhydride combustion*

Figure 5.14 shows the phthalic anhydride conversion on the Co-Mg-O/Al₂O₃ catalysts that the amount of magnesium is fixed at 1 wt%, while the amount of cobalt is varied to find the optimum amount of cobalt. It was found that 8Co1MgO/Al₂O₃ shows the best conversion, which increases from 30 to 85% in the temperature range of 200 to 300°C. After that it slightly increases to 90% at 550°C. On the other hand, 10Co1MgO/Al₂O₃, 9Co1MgO/Al₂O₃, 7Co1MgO/Al₂O₃ and 6Co1MgO/Al₂O₃ exhibit the conversion close to each other, about 20 to 85%. The catalytic activity of these catalyst is in the order of 8Co1MgO/Al₂O₃ > 10Co1MgO/Al₂O₃ > 6Co1MgO/Al₂O₃ > 9Co1MgO/Al₂O₃ > 7Co1MgO/Al₂O₃.

- *Maleic anhydride combustion*

The catalytic activity of Co-Mg-O/Al₂O₃ catalysts that the amount of magnesium is fixed at 1 wt%, while the amount of cobalt is varied to find the optimum amount of cobalt, is shown in Figure 5.15. The 8Co1MgO/Al₂O₃ catalyst shows the best conversion, which enhances from 10 to 98% with reaction temperature from 200 to 550°C. While 10Co1MgO/Al₂O₃, 9Co1MgO/Al₂O₃, 7Co1MgO/Al₂O₃ and 6Co1MgO/Al₂O₃ show the conversion about 5 to 90%. The catalytic activity of the catalyst decreases in the order of 8Co1MgO/Al₂O₃ > 10Co1MgO/Al₂O₃ > 6Co1MgO/Al₂O₃ > 9Co1MgO/Al₂O₃ > 7Co1MgO/Al₂O₃.

The research finds that the optimum amount of cobalt for phthalic anhydride and maleic anhydride combustion is around 8 wt%. The amount of cobalt loading strongly affects the adsorption of acidic reactant and the catalytic acidity that controlled the catalytic activity. In case of excess cobalt loading, the catalyst acidity increases while the adsorption of acidic reactant decreases that made the catalytic activity decreases, because the ability to adsorb the acidic reactant of magnesium is hidden by cobalt. On the other hand, lean cobalt loading affects the activity of the catalyst to decrease. The catalytic activity decreased because the leanness of active

site to react with the anhydride and magnesium is not able to catalyze the reaction by itself.



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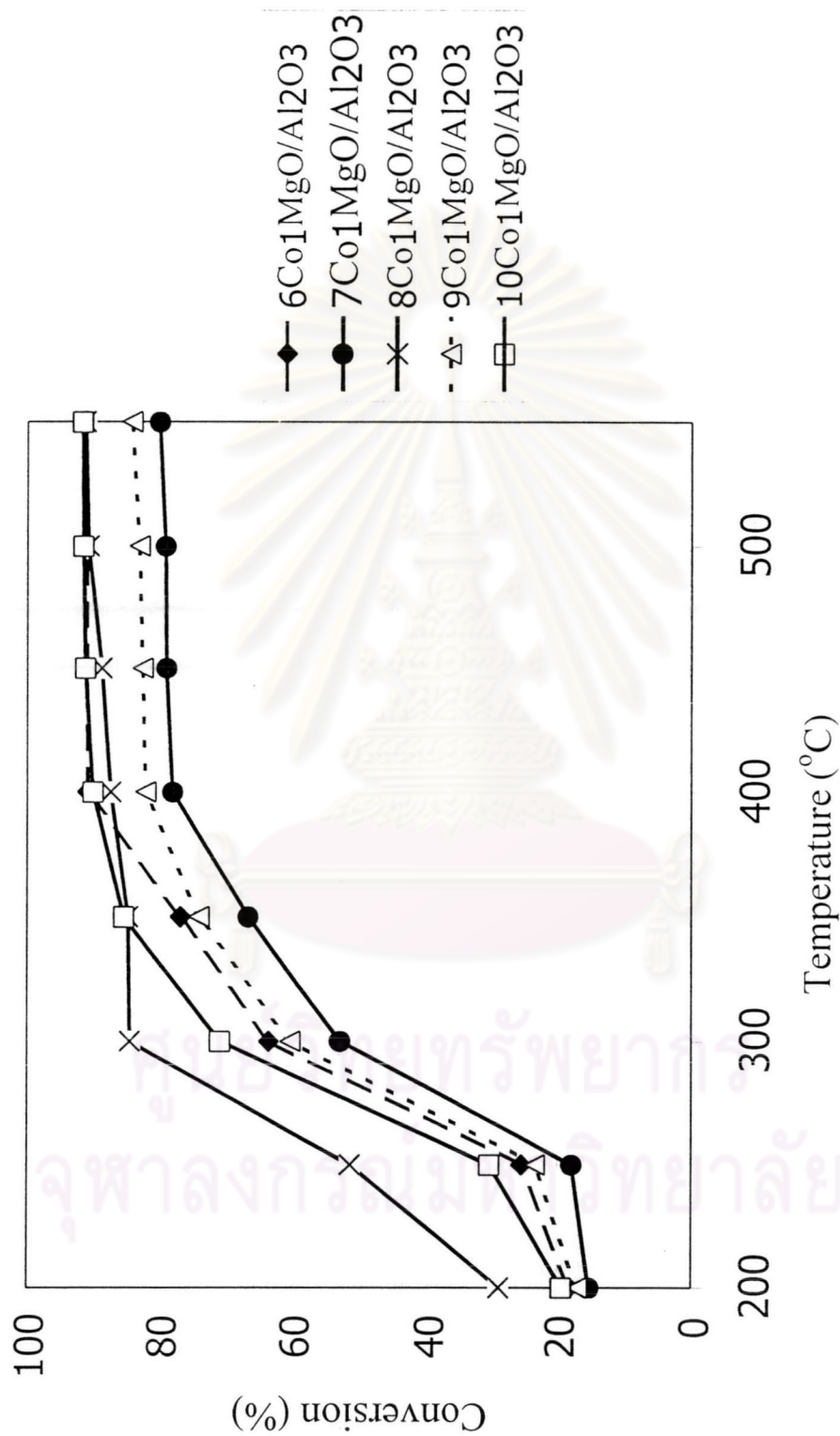


Figure 5.14 Catalytic activity of Co-Mg-O/Al₂O₃ catalysts that fixed Mg at 1 wt% with various Co wt% for phthalic anhydride combustion with feed contains 0.05 mol% phthalic anhydride in air

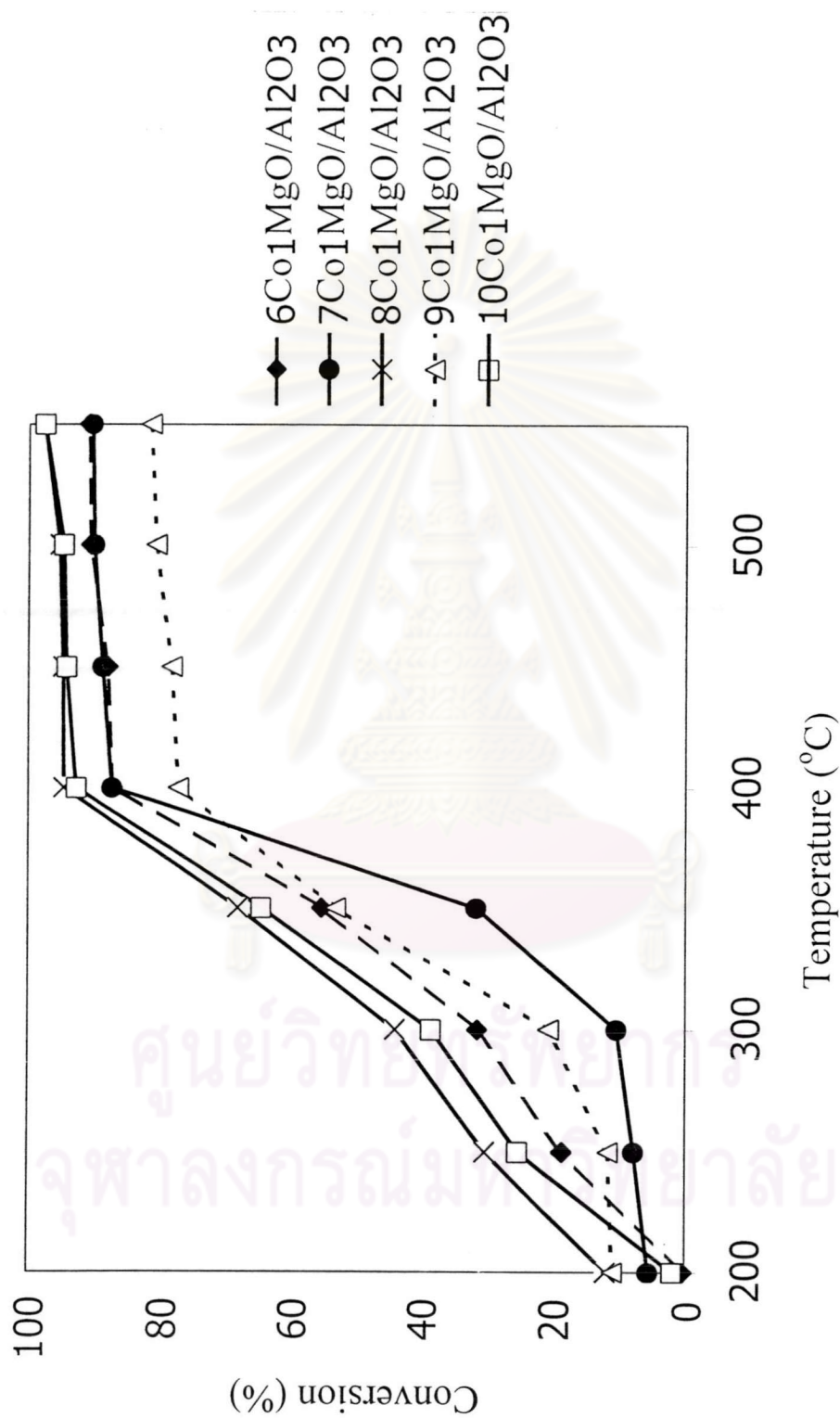


Figure 5.15 Catalytic activity of Co-Mg-O/Al₂O₃ catalysts that fixed Mg at 1 wt% with various Co wt% for maleic anhydride combustion with feed contains 0.05 mol% maleic anhydride in air