CHAPTER V

RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two parts, the catalytic oxidation reaction of 1-propanol and 2-propanol and the characterization of fresh and used catalysts.

5.1 Catalytic oxidation reaction

In this work, the effect of catalyst supports, TiO_2 and Al_2O_3, and loading sequence of cobalt and magnesium on catalytic deactivation are interested. Due to scarce deactivation information of CoMgTi and CoMgAl catalysts, in this research the stability of 8CoMgTi, 1Mg8CoTi, co-8Co1MgTi, 8Co1MgAl, 1Mg8CoAl, and co-8Co1MgAl catalysts are studied using oxidation reactions of 1-propanol and 2-propanol at 300° C and 500°C for 48 h as test reactions.

5.1.1 1-Propanol oxidation at 300°C for 48 h.

- 8Co1MgTi catalyst

Figure 5.1a shows the activity of 8Co1MgTi catalyst over 1-propanol oxidation for 48 h. The conversion of 1-propanol slightly decreases from 45% to 40% after 20 h of reaction and then gradually decreases to 36% at 48 h of reaction. Propionaldehyde is main product for this reaction and its selectivity does not show any deviation from initiation of this reaction, the selectivity of propanol for this reaction was about 73%. Traces of other reaction products, i.e., carbon dioxide, ethylene, propylene, and formaldehyde, are produced.

- 1Mg8CoTi catalyst

The behavior of 1Mg8CoTi catalyst for 1-propanol oxidation is described in Figure 5.1b. The conversion of 1-propanol at the first 2 h of experiment is 26% and moderately decreases to 21% after 11 h and then constant at that point until 29 h, the conversion slightly decreases to 15% and stable at this level through 48 h of reaction. The selectivity of the main product, propionaldehyde is ca. 85% for all period of reaction.

- co-8Co1MgTi catalyst

The conversion of 1-propanol is maintained at ca. 45% parallels to the propionaldehyde selectivity, the main product which is constant at ca. 94% through 48 h of experiment as describes in Figure 5.1c.

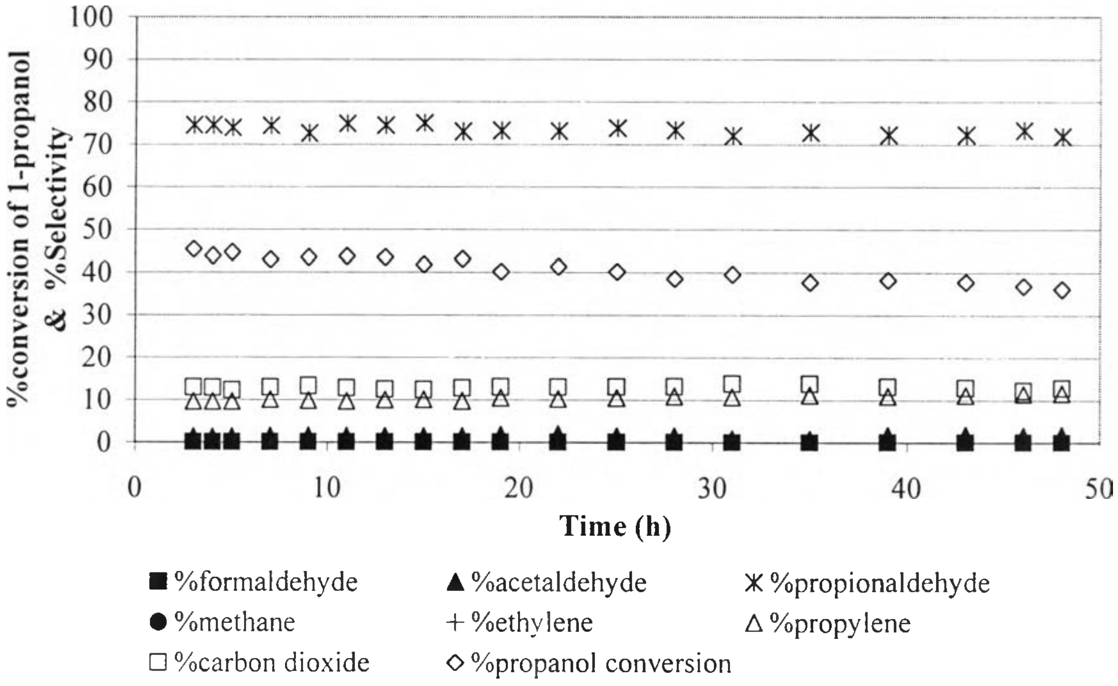

Figure 5.1a Catalytic property of 8Co1MgTi catalyst in the 1-propanol oxidation at 300°C for 48 h.

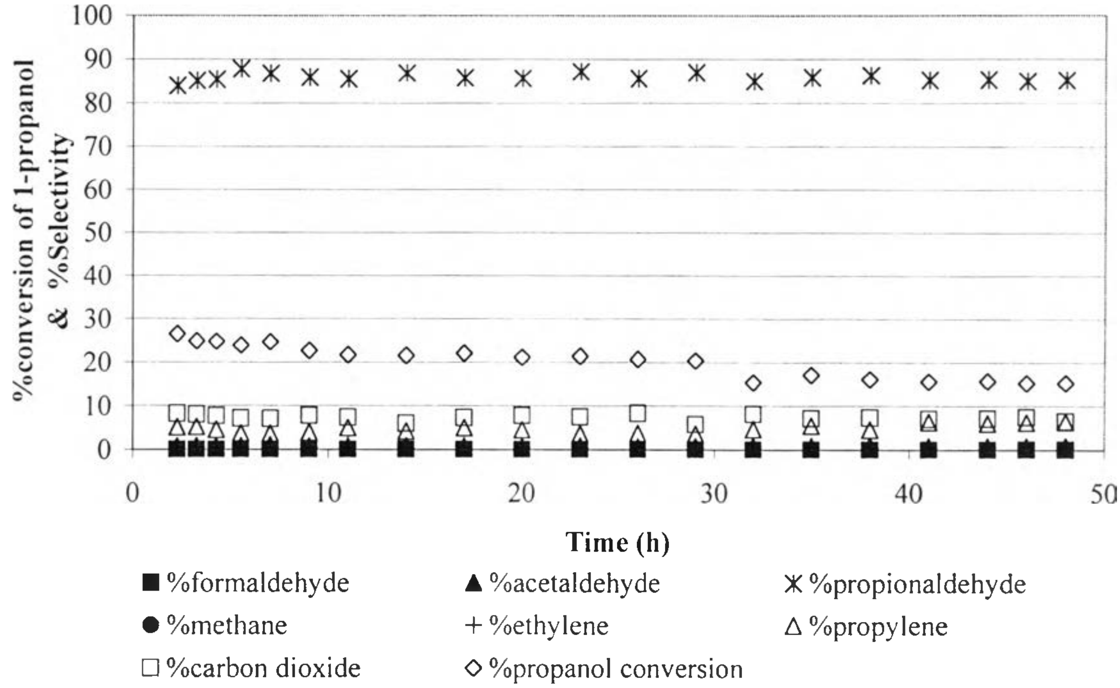

Figure 5.1b Catalytic property of 1Mg8CoTi catalyst in the 1-propanol oxidation at 300°C for 48 h.

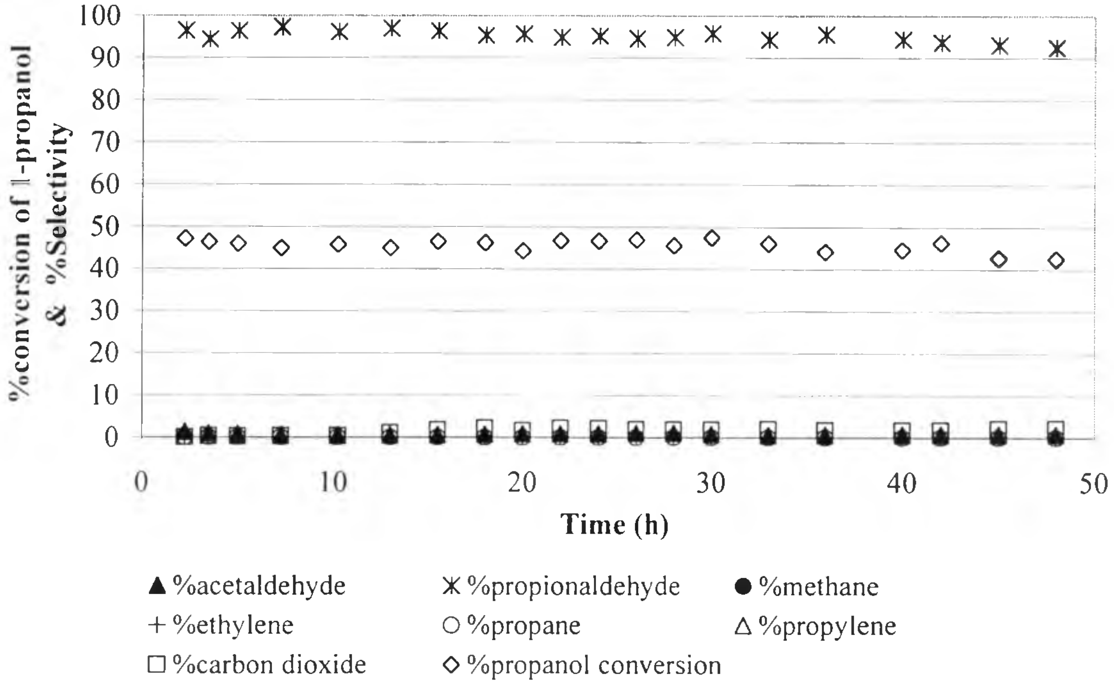

Figure 5.1c Catalytic property of co-8Co1MgTi catalyst in the 1-propanol oxidation at 300°C for 48 h.

- 8Co1MgAl catalyst

The catalytic property of 8Co1MgAl catalyst on 1-propanol oxidation at 300°C is illustrated in Figure 5.2a. The conversion of 1-propanol gradually decreases from 33% to 29% within the first 9 h and then stables at this value until 48 h of reaction. Similar to the selectivity of the main product of this catalytic oxidation, propionaldehyde, which decreases from 78% to 70% in 9 h and maintains at this level. Also there are some other reaction products such as propylene and carbon dioxide observed.

- 1Mg8CoAl catalyst

The result of catalytic reaction of 1-propanol on 1Mg8CoAl catalyst is shown in Figure 5.2b. At 24 h of reaction, 1-propanol conversion decreases from 34% to 32% and then settles at this value until the end of the reaction. Selectivity of products in this reaction remains constant at 70%, 20% and 10% for propionaldehyde, propylene and carbon dioxide respectively.

- co-8Co1MgAl catalyst

Figure 5.2c demonstrates the catalytic deactivation characteristics of co-8Co1MgAl in 1-propanol oxidation. After begin the reaction for 5 h, the conversion of 1-propanol rapidly decreases from ca. 50% to ca. 30% at 12 h and remains at this level until 48h. On the contrary, selectivity of main product, propionaldehyde is steadily increases from ca. 60% at first 2 h to ca. 75% after 10 h of reaction. Traces amount of acetaldehyde and carbon dioxide are detected.

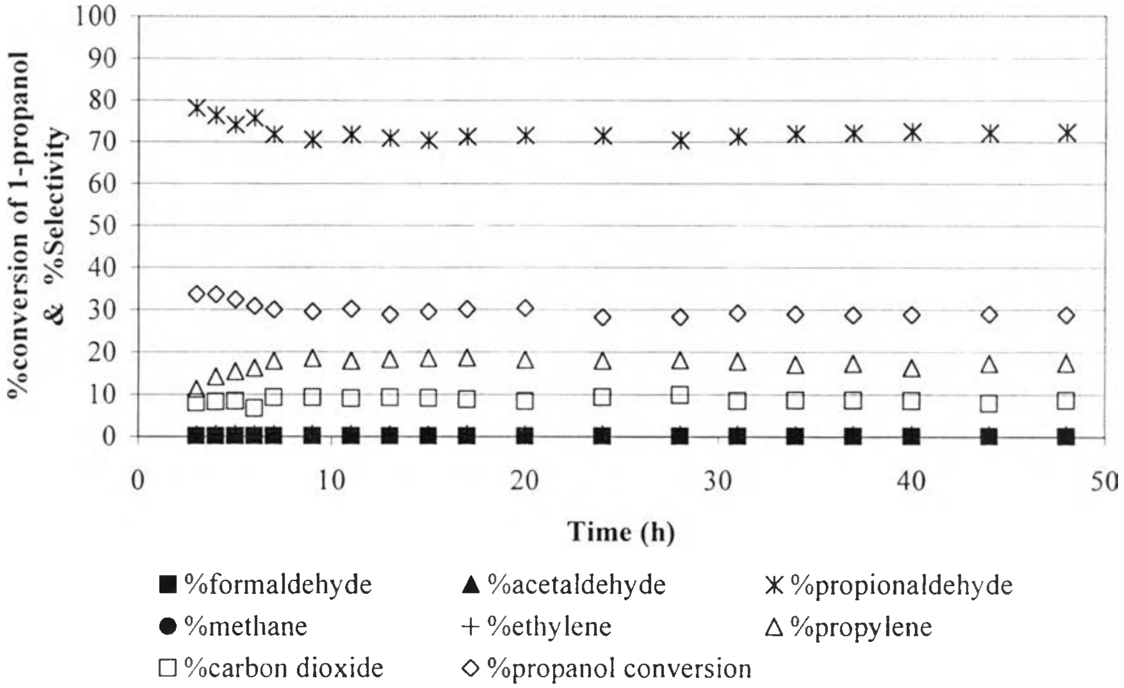

Figure 5.2a Catalytic property of 8Co1MgAl catalyst in the 1-propanol oxidation at 300°C for 48 h.

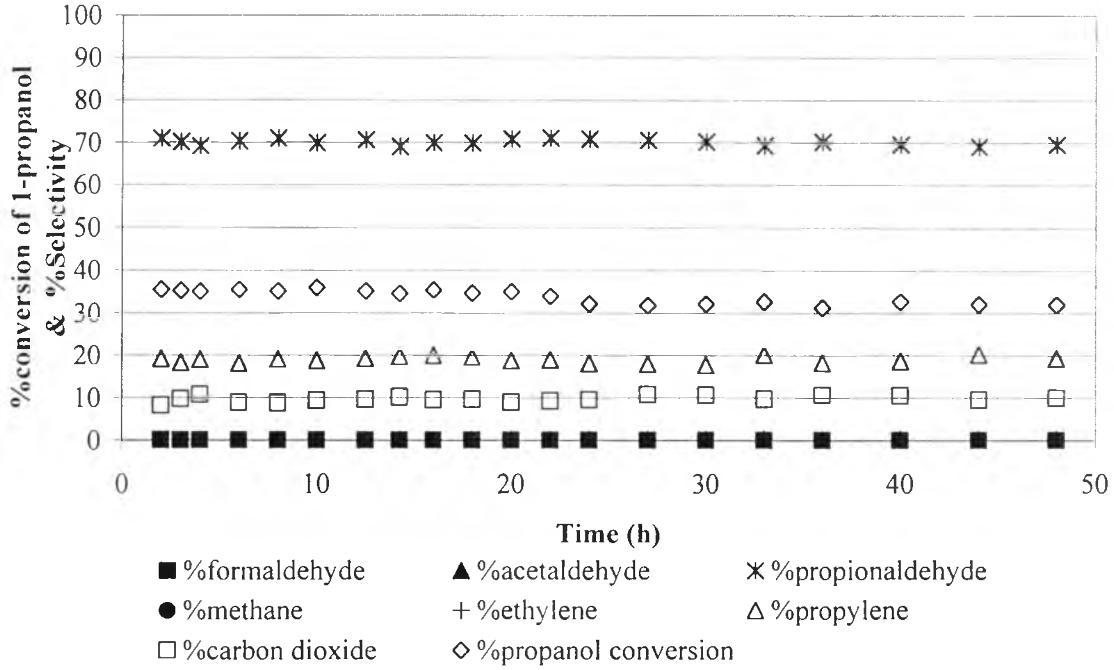

Figure 5.2b Catalytic property of 1Mg8CoAl catalyst in the 1-propanol oxidation at 300°C for 48 h.

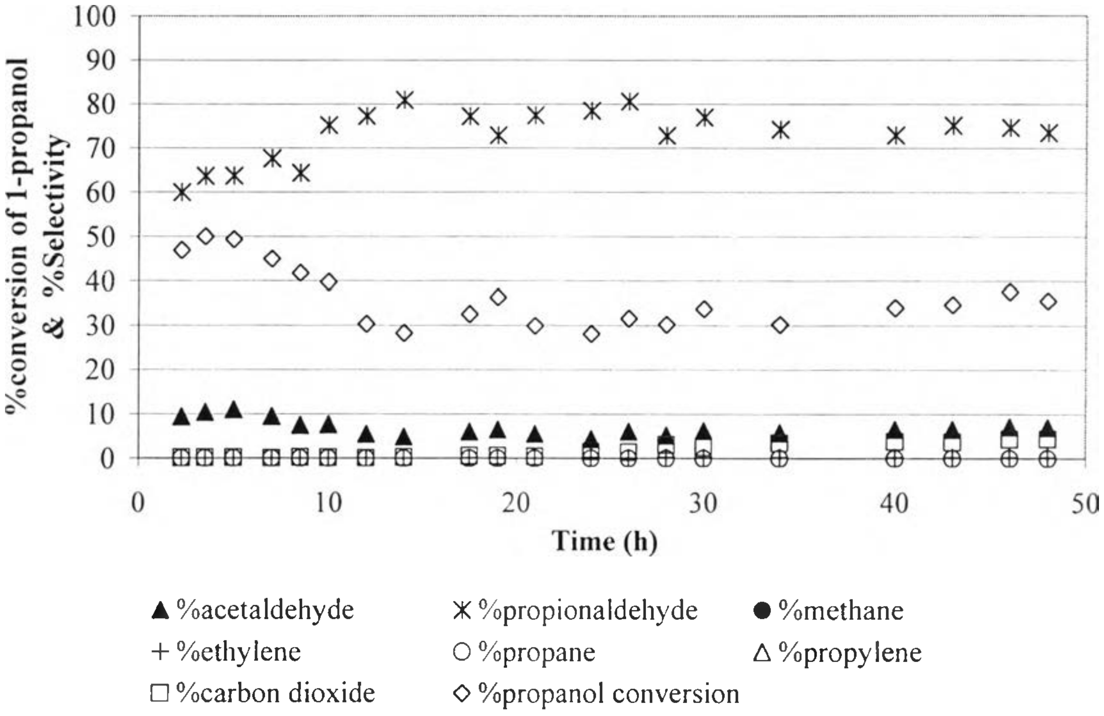

Figure 5.2c Catalytic property of co-8Co1MgAl catalyst in the 1-propanol oxidation at 300°C for 48 h.

5.1.2 2-Propanol oxidation at 300°C for 48 h.

- 8Co1MgTi catalyst

Figure 5.3a illustrates the catalytic activity of 2-propanol oxidation at 300°C. The conversion of 2-propanol slightly decreases from 52% during the first 3 h to 47%. After 6 h of reaction and continues settle at this point until 16 h then gradually decreases to 42% at 25% and constants at this value until 48 h of reaction. Main products of this reaction are propylene and propionaldehyde with small amounts of carbon dioxide. Selectivity of propylene and propionaldehyde through 48 h are 60% and 35% respectively.

- 1Mg8CoTi catalyst

The 2-propanol conversion starts to decrease at 3 h of reaction from 51% to ca. 40% after 25 h and then stables at this level until 48 h of reaction as describes in

Figure 5.3b. Propylene and propionaldehyde are main products of this reaction with small amount of carbon dioxide. The selectivity of propionaldehyde slightly decreases from ca. 61% at first 3 h to ca. 50% after 31 h of reaction. On the other hand, selectivity of propylene gradually increases from ca. 33% at 3 h of reaction to ca. 43% after 29 h of experiment.

- **co-8Co1MgTi catalyst**

The result of the catalytic oxidation of 2-propanol on co-8Co1MgTi is shown in Figure 5.3c. The conversion of 2-propanol is quite constant at ca. 70% through all 48 h of reaction. The main product of this reaction is propionaldehyde. The selectivity of propionaldehyde is 95% at first 2 h of reaction after that decreases to ca. 90% at 7 h of reaction and then settles at this value until 48 h.

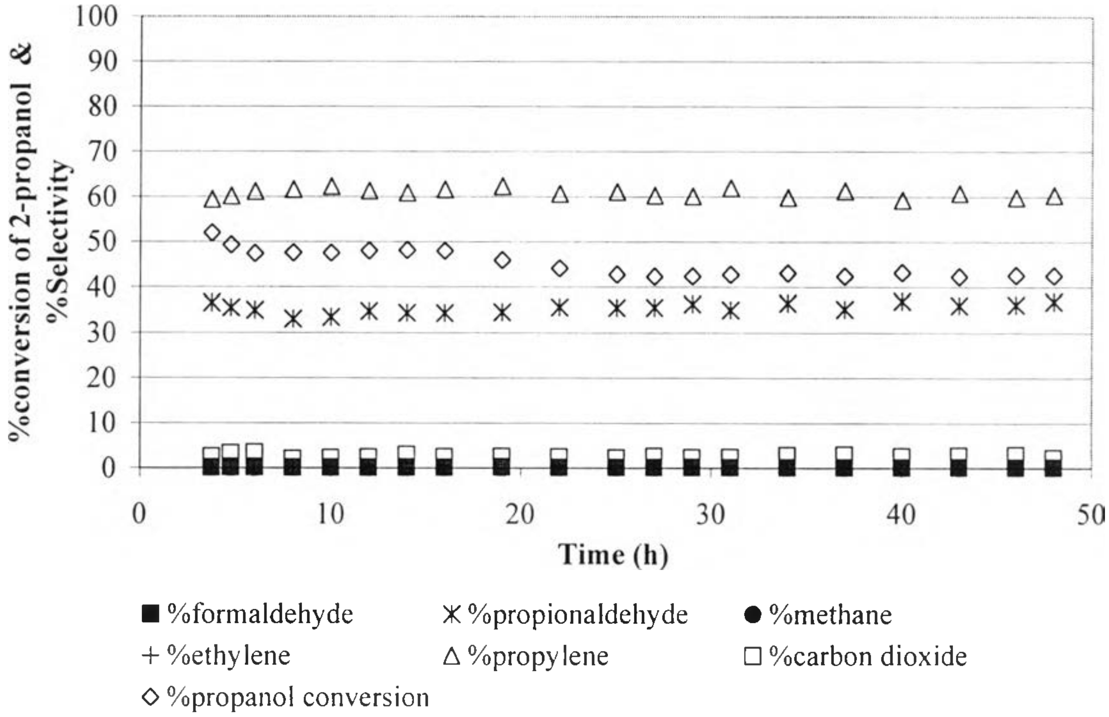

Figure 5.3a Catalytic property of 8Co1MgTi catalyst in the 2-propanol oxidation at 300°C for 48 h.

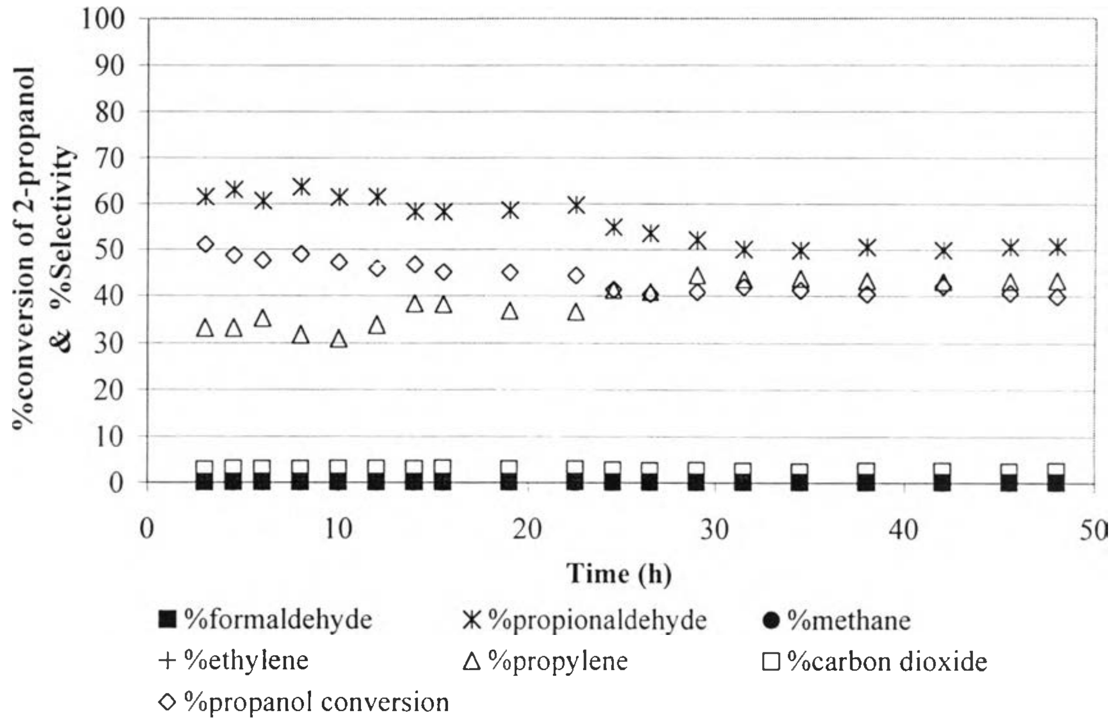

Figure 5.3b Catalytic property of 1Mg8CoTi catalyst in the 2-propanol oxidation at 300°C for 48 h.

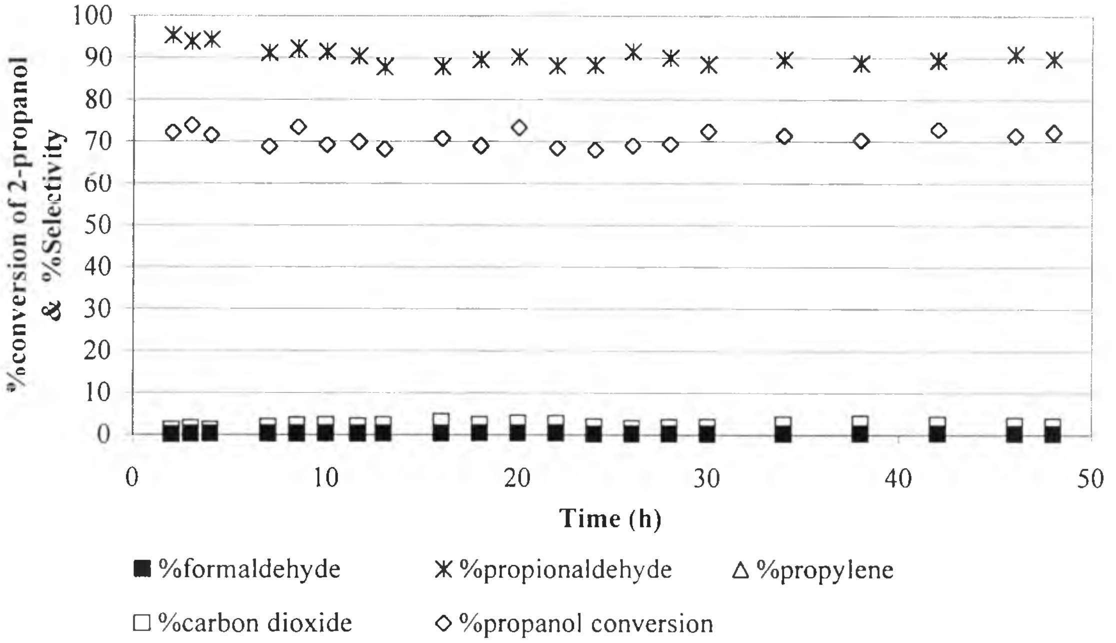

Figure 5.3c Catalytic property of co-8Co1MgTi catalyst in the 2-propanol oxidation at 300°C for 48 h.

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- 8Co1MgAl catalyst

Figure 5.4a demonstrates the catalytic property of 8Co1MgTi in the 2-propanol oxidation. Conversion of 2-propanol stables at 96% through all 48 h of reaction. The main product of this reaction is propylene with a small amount of propionaldehyde. Propylene selectivity is 90% in first 15 h of reaction and then decreases to ca. 90% at 17 h. After that propylene selectivity remains constants at that value until 48 h of reaction.

- 1Mg8CoAl catalyst

The result of the catalytic oxidation of 2-propanol on 1Mg8CoAl catalyst is shown in Figure 5.4b. The conversion of 2-propanol remains constant at ca. 95% through 48 h of reaction. Propylene and propionaldehyde are main products for this reaction. Propylene and propionaldehyde selectivity are ca. 63% and 35% respectively for all 48 h of experiment.

- co-8Co1MgAl catalyst

The behavior of the 8Co1MgAl catalyst in 2-propanol oxidation at 300°C is described in Figure 5.4c. The conversion of 2-propanol is constant at 100% for the first 20 h of reaction after that slightly decreases to ca. 88% at 26 h and then stables at that level until 48 h of reaction. The selectivity of the main product, propionaldehyde is ca. 90% for first 26 h then slightly decreases and remains constant at 82% after 39 h of reaction. Small amounts of propylene and carbon dioxide are observed.

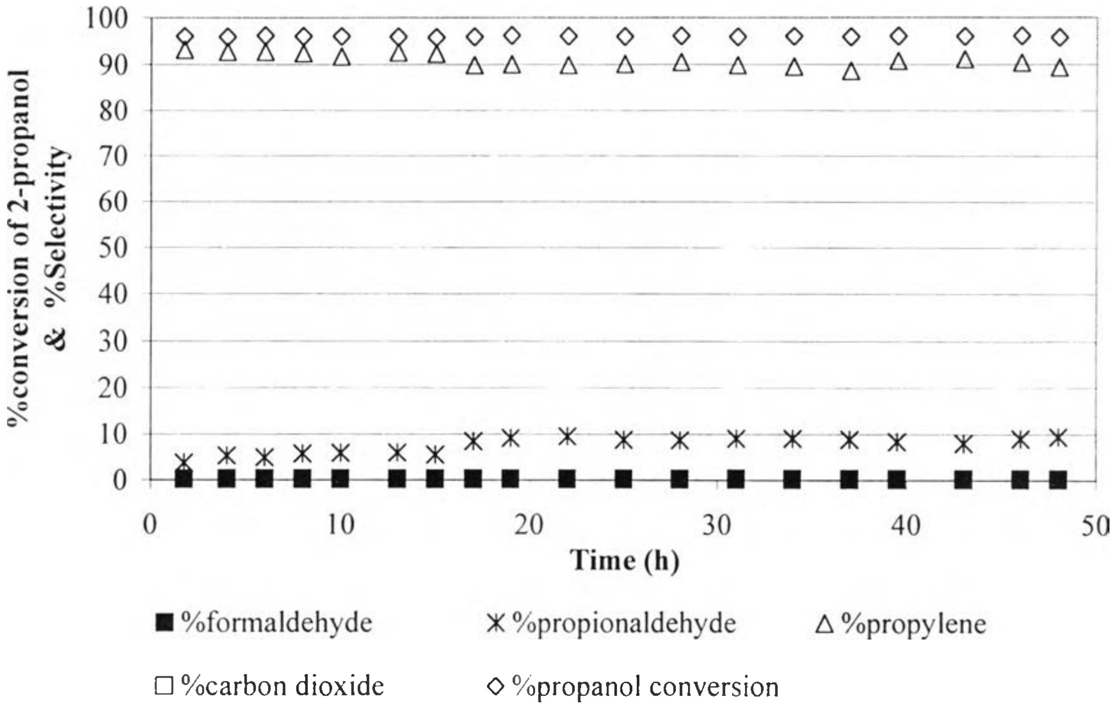

Figure 5.4a Catalytic property of 8Co1MgAl catalyst in the 2-propanol oxidation at 300°C for 48 h.

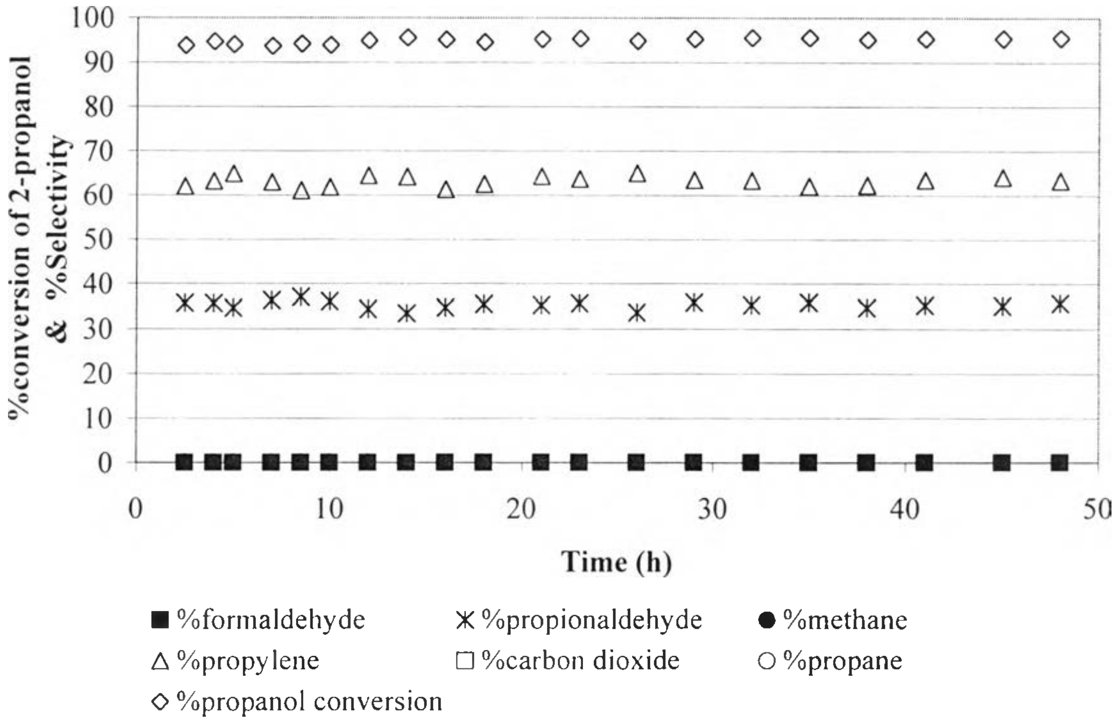

Figure 5.4b Catalytic property of 1Mg8CoAl catalyst in the 2-propanol oxidation at 300°C for 48 h.

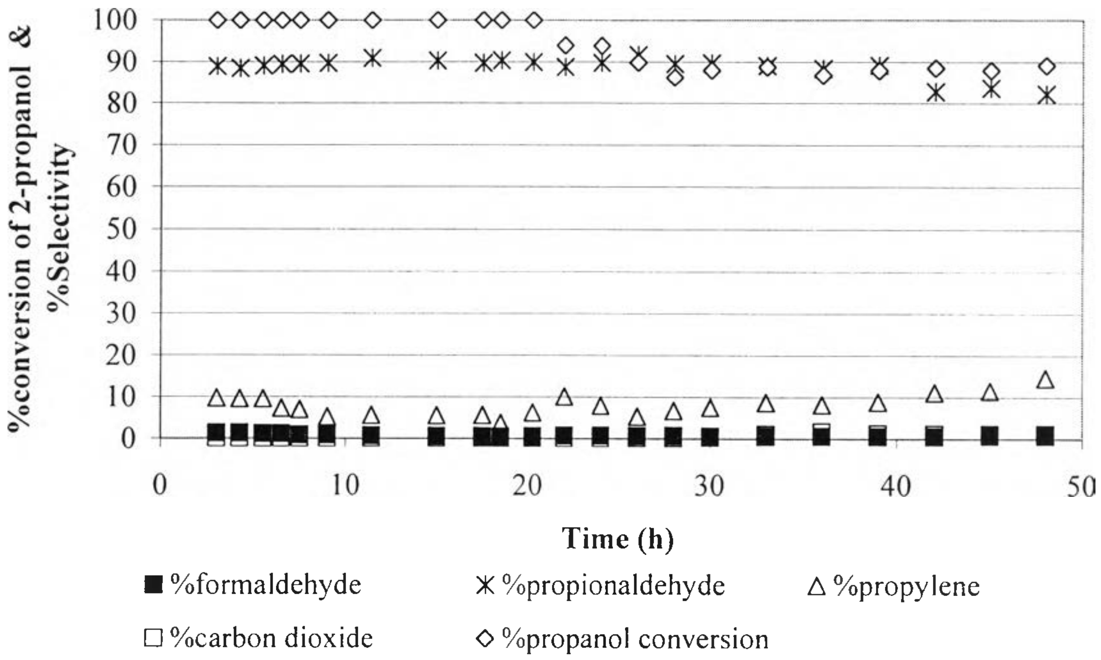

Figure 5.4c Catalytic property of co-8Co1MgAl catalyst in the 2-propanol oxidation at 300°C for 48 h.

5.1.3 1-Propanol oxidation at 500°C for 48 h.

- 8Co1MgTi catalyst

The stability test result of 8Co1MgTi catalyst on 1-propanol oxidation is demonstrated in Figure 5.5a. Conversion of 1-propanol for this reaction is about 73% through 48 h of experiment. The main product of this reaction is propionaldehyde with small amounts of carbon dioxide, acetaldehyde, ethylene etc. Propionaldehyde selectivity is constant at 70% for all 48 h of reaction.

- 1Mg8CoTi catalyst

Figure 5.5b illustrates the catalytic activity of 1Mg8CoTi catalyst on 1-propanol oxidation reaction. The 1-propanol conversion is stable at ca. 80% for all 48 h of reaction. Propionaldehyde is the main product for this reaction, also some traces of carbon dioxide, acetaldehyde, ethylene, propylene, formaldehyde, propane and methane. Selectivity of propionaldehyde is stable at the average level of 55% through 48 h of reaction.

- co-8Co1MgTi catalyst

The behavior of co-8Co1MgTi catalyst is shown in Figure 5.5c. The conversion of 1-propanol is ca. 65% at first 18 h of experiment then the conversion falls to 60% when pass 22 h of reaction and then maintain at this level until 48 h of reaction. The main product of this reaction is propionaldehyde with small amounts of carbon dioxide, ethylene, acetaldehyde etc. On the average, propionaldehyde selectivity in first 16 h is 67% and then slightly increases to 80% at 48 h of reaction.

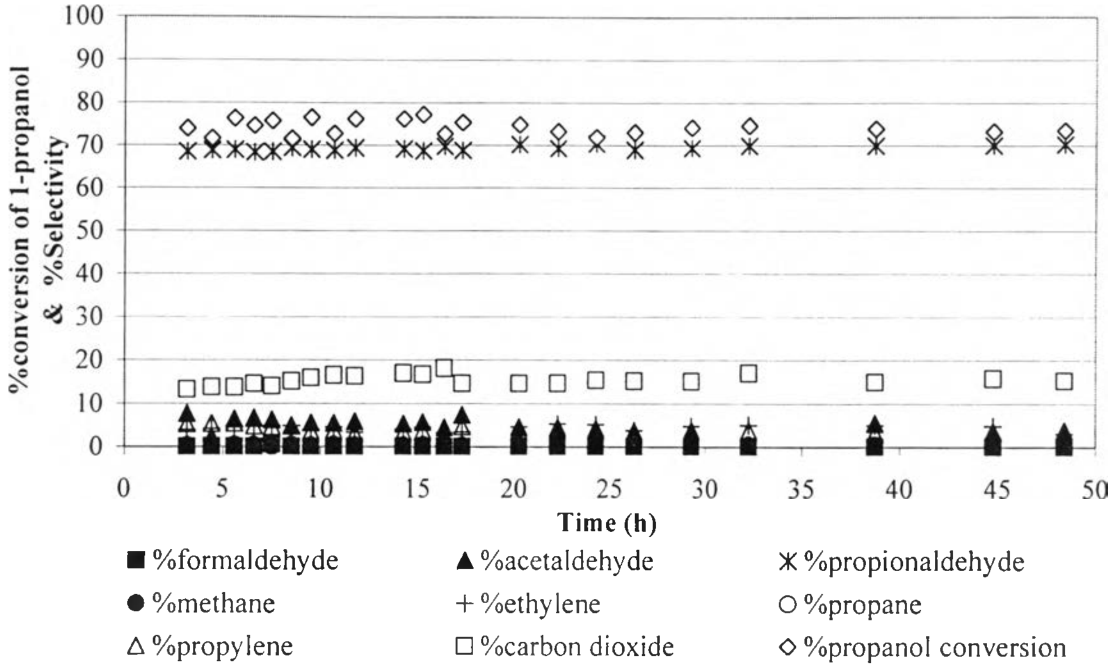

Figure 5.5a Catalytic property of 8Co1MgTi catalyst in the 1-propanol oxidation at 500°C for 48 h.

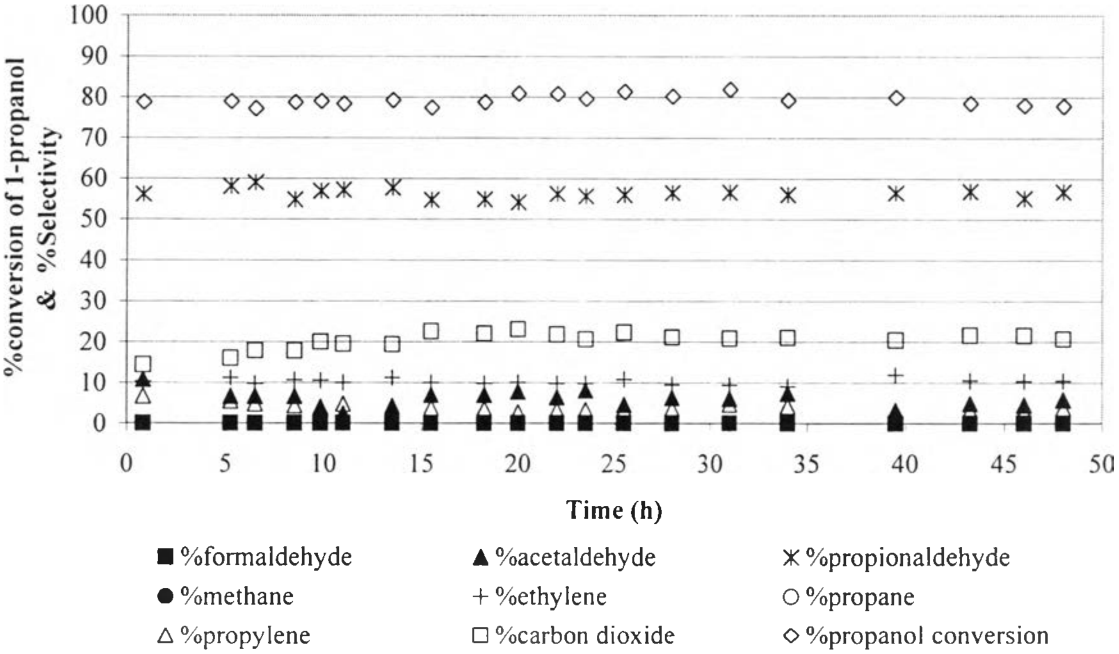

Figure 5.5b Catalytic property of 1Mg8CoTi catalyst in the 1-propanol oxidation at 500°C for 48 h.

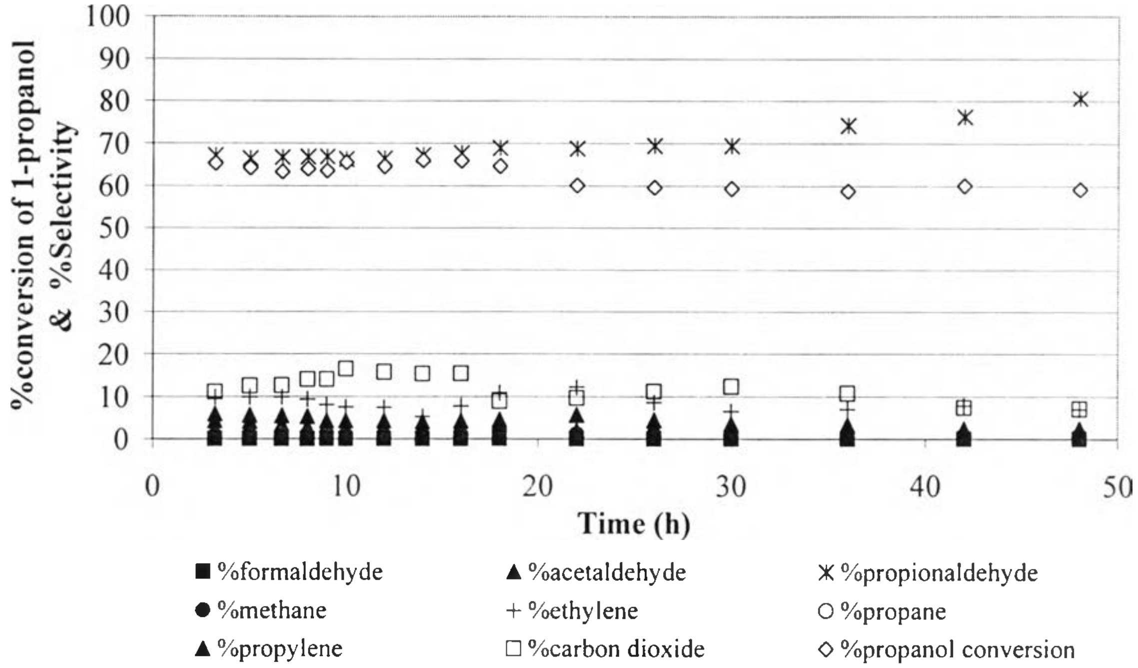

Figure 5.5c Catalytic property of co-8Co1MgTi catalyst in the 1-propanol oxidation at 500°C for 48 h.

- **8Co1MgAl catalyst**

The catalytic property of 8Co1MgAl catalyst is describes in Figure 5.6a. Conversion of 1-propionaldehyde is 100% in the first 6 h after that it slightly decreases to ca. 80% at 21 h of reaction and keeps at this value until 36 h pass then gradually decreases to ca. 70% at 48 h of reaction. The main products of this reaction are propionaldehyde and acetaldehyde with some traces of propylene, carbon dioxide, ethylene, methane, propane and formaldehyde. During the first 3 h of reaction, selectivity of propionaldehyde is 5.6% then gradually increases to 48% at 10 h and stay on this level until 25 h after that propionaldehyde selectivity slightly increases to ca. 62% at 48 h of reaction. Unlike propionaldehyde, acetaldehyde selectivity decreases from 47% at initial to ca. 20% in 13 h and settles at this value until 42 h pass, its selectivity then falls down to 11% at 48 h of reaction.

- 1Mg8CoAl catalyst

The result of catalyst stability test of 1Mg8CoAl is illustrated in Figure 5.6b. The conversion of 1-propanol rapidly decreases from 98% at initial to 68% at 18 h of reaction and slightly decreases to 62% at 40 h then swiftly decreases to ca. 45% at 48 h of reaction. The main products of this reaction in first 20 h are propionaldehyde and acetaldehyde after that only propionaldehyde is the main product. Also there are small amounts of other product i.e. propylene, ethylene. Propionaldehyde selectivity gradually rises from 31% at 4 h to ca. 90% at 48 h of reaction whereas acetaldehyde selectivity falls from 51% at initial to 3% when 48 h pass.

- co-8Co1MgAl catalyst

Figure 5.6c demonstrates the behavior of co-8Co1MgAl catalyst in 1-propanol oxidation. Conversion of 1-propanaol rapidly decreases from 97% during the first 4 h to 73% at 9 h of reaction then stay at this level through out 48 h of reaction. During the first 3 h of reaction, selectivity of propylene is 43% while selectivity of propionaldehyde is 25%, 1 hour later, propylene selectivity speedily falls to 17% whereas propionaldehyde selectivity rises to 62%. Subsequently, propionaldehyde selectivity continuously increases to 70% and settles at that value until 48 h of reaction. In contrast, selectivity of acetaldehyde slightly decreases to 4% and stables at this level though 48 h.

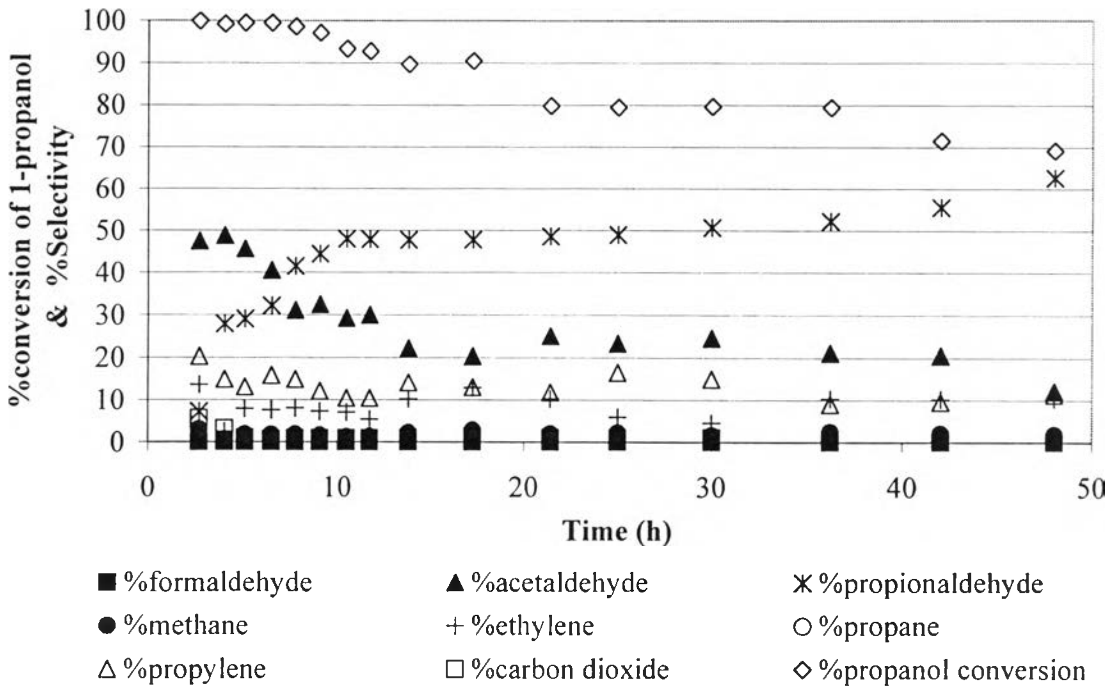

Figure 5.6a Catalytic property of 8Co1MgAl catalyst in the 1-propanol oxidation at 500°C for 48 h.

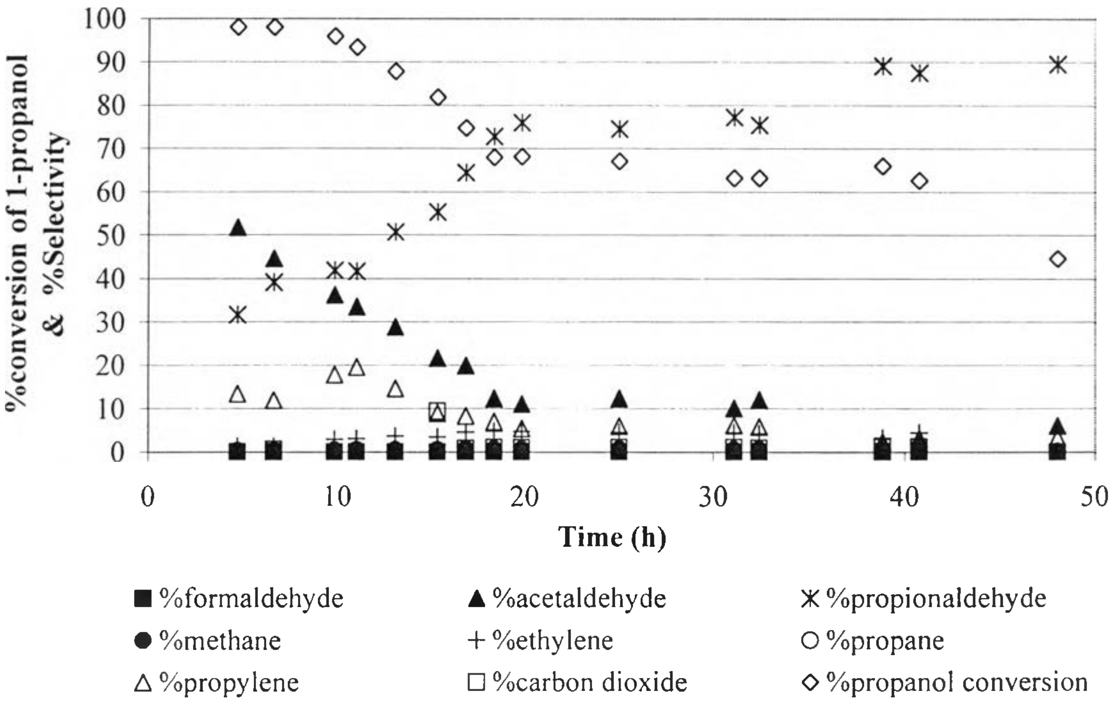

Figure 5.6b Catalytic property of 1Mg8CoAl catalyst in the 1-propanol oxidation at 500°C for 48 h.

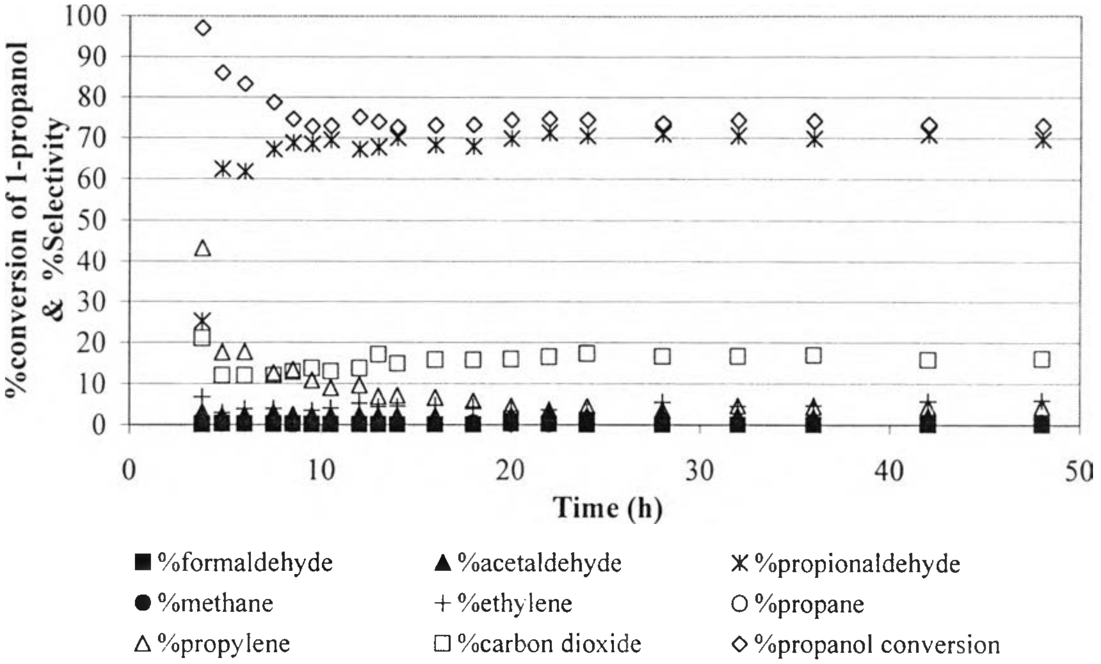

Figure 5.6c Catalytic property of co-8Co1MgAl catalyst in the 1-propanol oxidation at 500°C for 48 h.

5.1.4 2-Propanol oxidation at 500°C for 48 h.

- 8Co1MgTi catalyst

The catalytic property of 8Co1MgTi catalyst on 2-propanol oxidation is described in Figure 5.7a. In the first 29 h of experiment, the conversion of 2-propanol slightly raises from 74% to 79% then rapidly increases to 90% and stay at this value through out 48 h of reaction. Selectivity of propionaldehyde, the main product of this reaction is 80% in first 29 h after that it gradually decreases to 55% at 48 h of reaction. While propionaldehyde selectivity decreases, selectivity of propylene increases from 12% to ca. 24%. Traces of other reaction products such as carbon dioxide, ethylene etc. can be detected.

- 1Mg8CoTi catalyst

The deactivation behavior of 1Mg8CoTi catalyst for 2-propanol oxidation is illustrated in Figure 5.7b. The conversion of 2-propanol gradually decreases from 100% at reaction initiation to the average level of 70% at 17 h of reaction. Main products of this reaction are propionaldehyde, propylene and acetaldehyde. In the first 3 h, propylene selectivity is 36% then rises to 43% after 5 h pass and stays at this value until 48 h. Acetaldehyde selectivity slightly decreases from 43% to ca. 25% at 29 h of reaction and settles at this level through 48 h. On the contrary, propionaldehyde selectivity gradually increases from 16% to 27% when 20 h of reaction pass then constants at this value until 48 h.

- co-8Co1MgTi catalyst

Figure 5.7c demonstrates the catalytic activity of co-8Co1MgTi catalyst for 2-propanol oxidation reaction. The average conversion of 2-propanol in the first 42 h is 80% and then decreases to 76% at 48 h of reaction. Selectivity of propionaldehyde, main product of this reaction is 83% on average for first 42 h after that the selectivity increases to 87% at 48 h of experiment. There are also small amounts of other reaction products such as propylene, carbon dioxide.

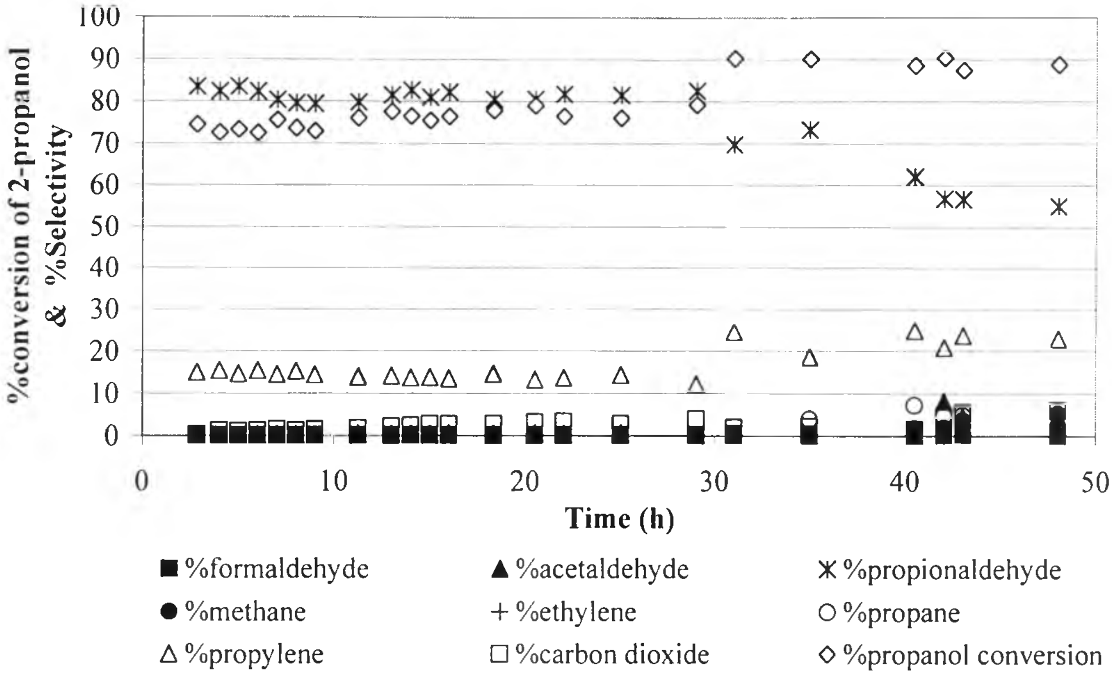

Figure 5.7a Catalytic property of 8Co1MgTi catalyst in the 2-propanol oxidation at 500°C for 48 h.

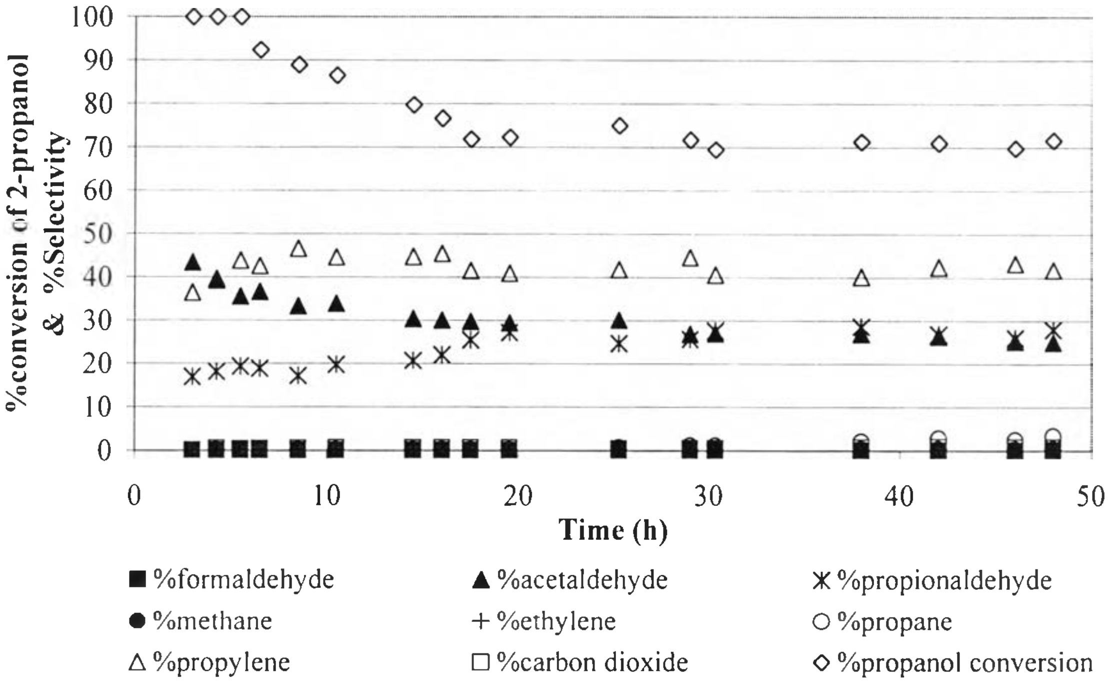

Figure 5.7b Catalytic property of 1Mg8CoTi catalyst in the 2-propanol oxidation at 500°C for 48 h.

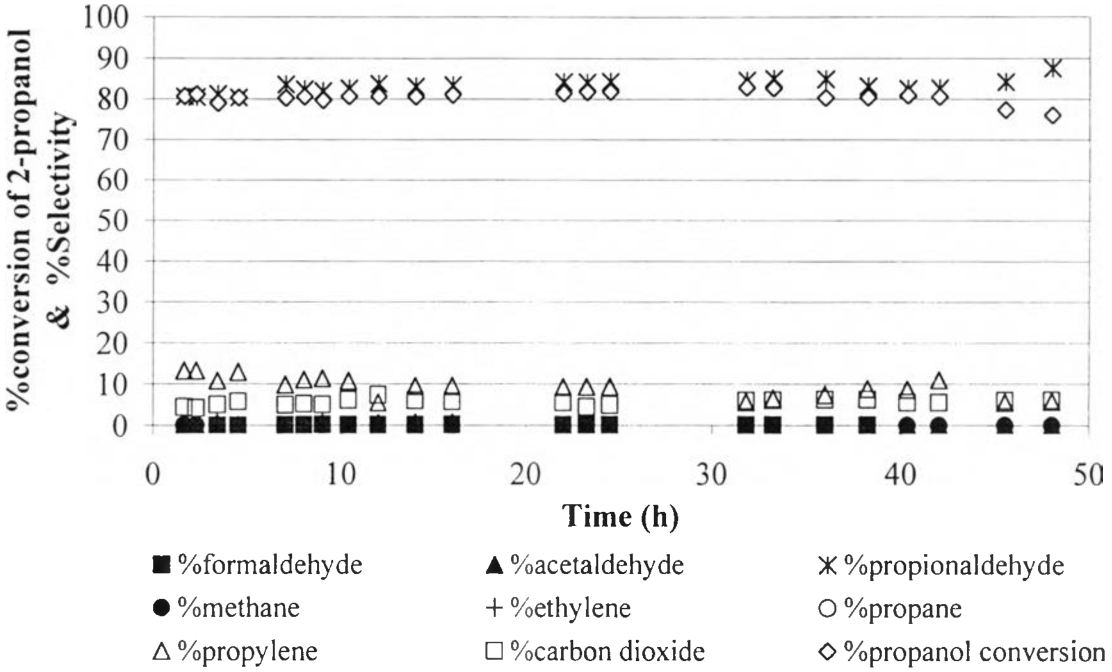

Figure 5.7c Catalytic property of co-8Co1MgTi catalyst in the 2-propanol oxidation at 500°C for 48 h.

- **8Co1MgAl catalyst**

The result of catalyst deactivation test of 8Co1MgAl on 2-propanol reaction at 500°C is shown in Figure 5.8a. In the first 10 h of reaction, 2-propanol conversion is 100% after that it slightly decreases to the average level of 75% at 17 h of reaction. Acetaldehyde and propionaldehyde are the main products in this reaction with small amounts of carbon dioxide, methane, ethylene, propane, formaldehyde and propylene. Acetaldehyde selectivity slightly decreases from 59% at initial to ca. 16% at 48 h whereas propionaldehyde selectivity gradually rises from 25% to 81% at 48 h of reaction.

- **1Mg8CoAl catalyst**

Figure 5.8b shows the stability of 1Mg8CoAl catalyst for 2-propanol oxidation reaction. The conversion of 2-propanol is 100% in first 8 h then it gradually decreases to the average level of 62% and constant until 48 h. Propylene and propionaldehyde are main products of this reaction. Propionaldehyde selectivity is 70% for first 6 h then delicately decreases to ca. 65% and settles at this value through 48 h of reaction. In case of propylene selectivity, it quite constants at 30% for all 48 h of experiment.

- **co-8Co1MgAl catalyst**

The behavior of co-8Co1MgAl catalyst on 2-propanol oxidation reaction at 500°C is described in Figure 5.8a. The conversion of 2-propanol gradually decreases from 98% in the first 3 h to ca. 80% at 28 h of reaction then constant at this level through out 48 h. The main products of this reaction are propylene and propionaldehyde with small amount of propane, carbon dioxide etc. Propionaldehyde selectivity is stable at an average level of 70% for the first 33 h then decreases to ca. 65% at 37 h and settles through 48 h. Propylene selectivity delicately decreases from 26% at initiation of reaction to 23% at 48 h of reaction.

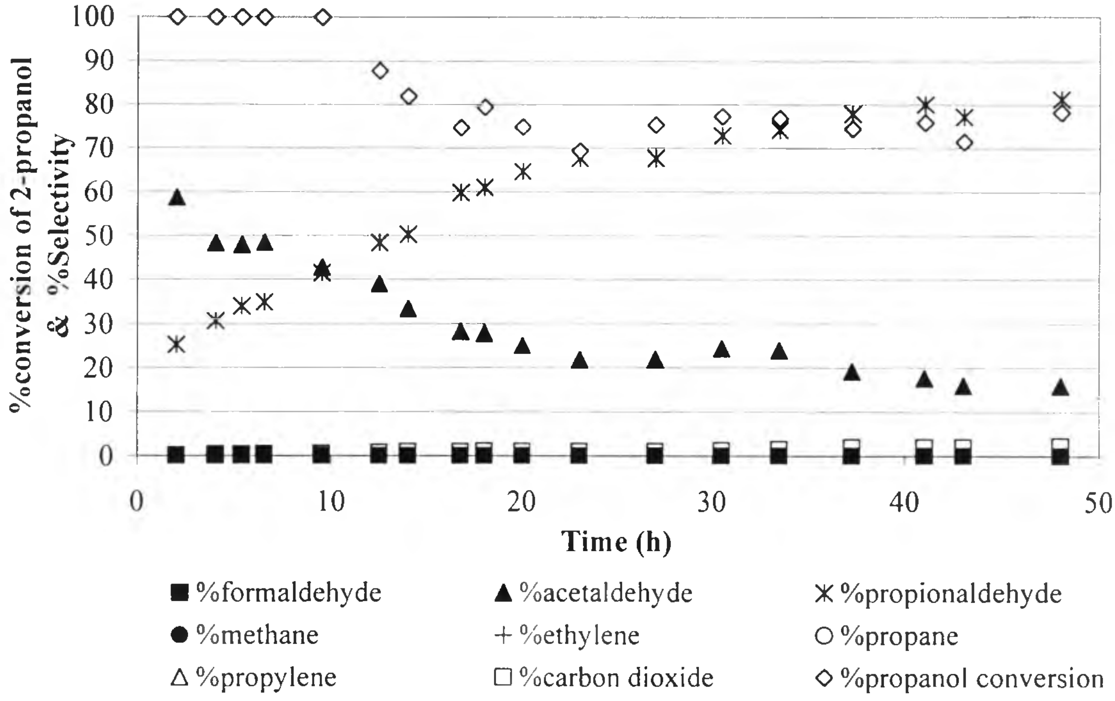

Figure 5.8a Catalytic property of 8Co1MgAl catalyst in the 2-propanol oxidation at 500°C for 48 h.

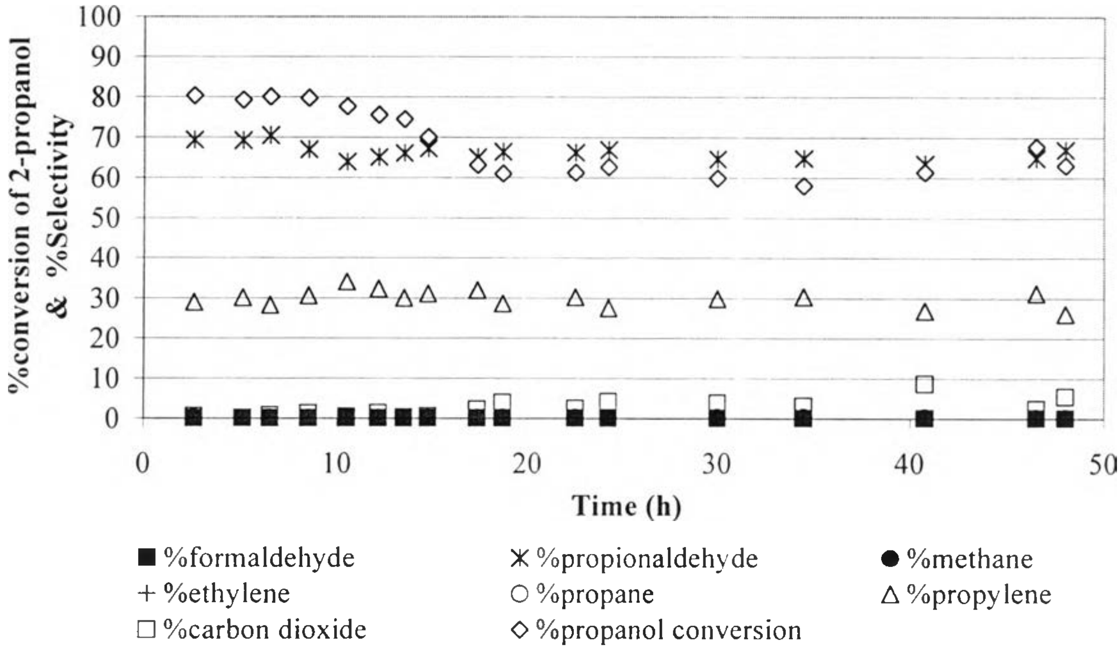

Figure 5.8b Catalytic property of 1Mg8CoAl catalyst in the 2-propanol oxidation at 500°C for 48 h.

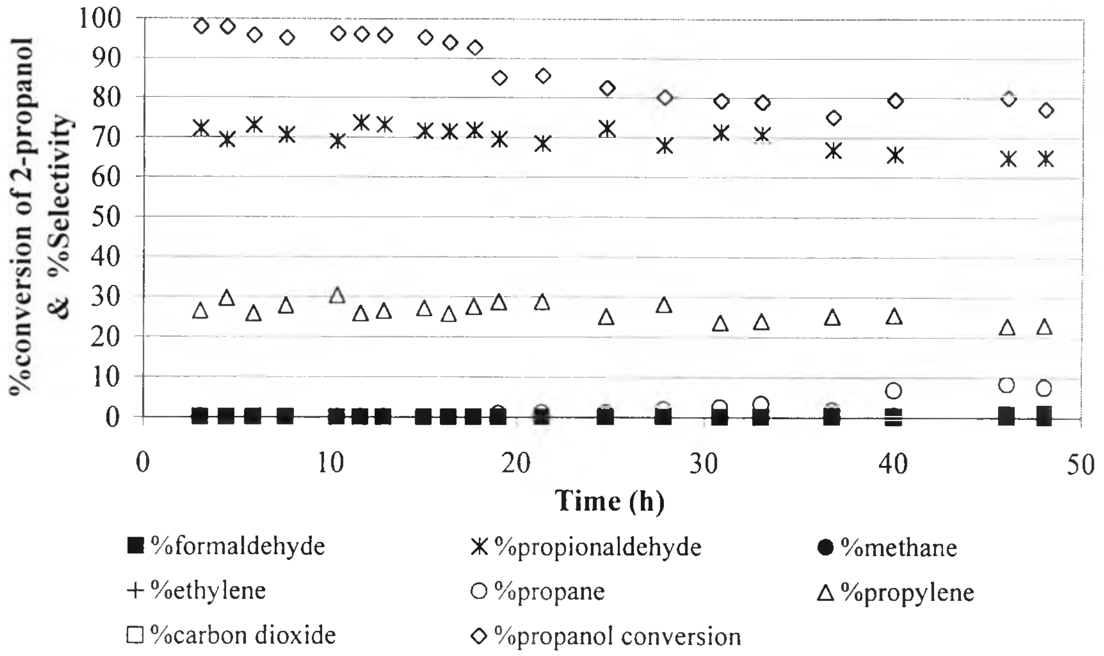

Figure 5.8c Catalytic property of co-8Co1MgAl catalyst in the 2-propanol oxidation at 500°C for 48 h.

5.1.4 Thermal stability test

In order to investigate the thermal stability of catalyst, this research uses high temperature to study deactivation behavior of the catalyst by calcination the catalyst at 700 and 800 °C for 7 days. Then the catalysts are used on 1-propanol and 2-propanol oxidation reaction.

The catalysts supported on TiO_2 are not tested because at this high temperature the TiO_2 (anatase) is known to be completely deactivated.

5.1.4.1 Catalytic reaction of 1-propanol

- co-8Co1MgAl calcined at 700°C for 7 days

Figure 5.9a demonstrates the catalytic activity of co-8Co1MgAl catalyst calcined at 700°C for 7 days in 1-propanol oxidation reaction. The conversion of 1-propanol rapidly increases from 1.5% to 97% when the reaction temperature increases from 200 to 350 °C and then slightly rises to 100% at 400°C. Selectivity of propionaldehyde is 78% at 200°C and swiftly falls to ca. 10% at 300°C then gradually decreases until disappear at 500°C. On the other hand, propylene selectivity rapidly increases from 18% to 87% when the reaction temperature rises from 200 to 300 °C.

- co-8Co1MgAl calcined at 800°C for 7 days

The catalytic property of co-8Co1MgAl catalyst calcined at 800°C for 7 days on 1-propanol oxidation is illustrated in Figure 5.9b. The 2-propanol conversion rapidly rises from 13% to 100% when the reaction temperature increases from 250 to 400 °C. Propylene is main product for this reaction. Even though the reaction temperature rises, its selectivity still stables at 90%. Traces of other reaction product such as propionaldehyde, carbon dioxide are detected.

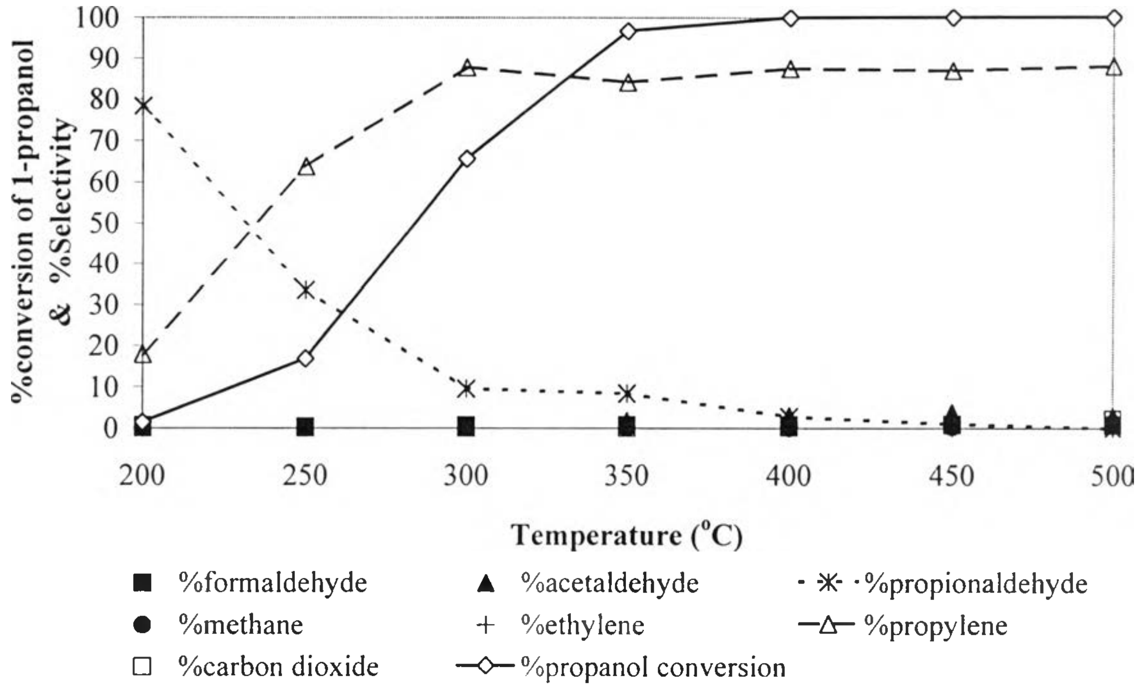

Figure 5.9a Catalytic property of co-8Co1MgAl catalyst calcined at 700°C for 7 days in the 1-propanol oxidation.

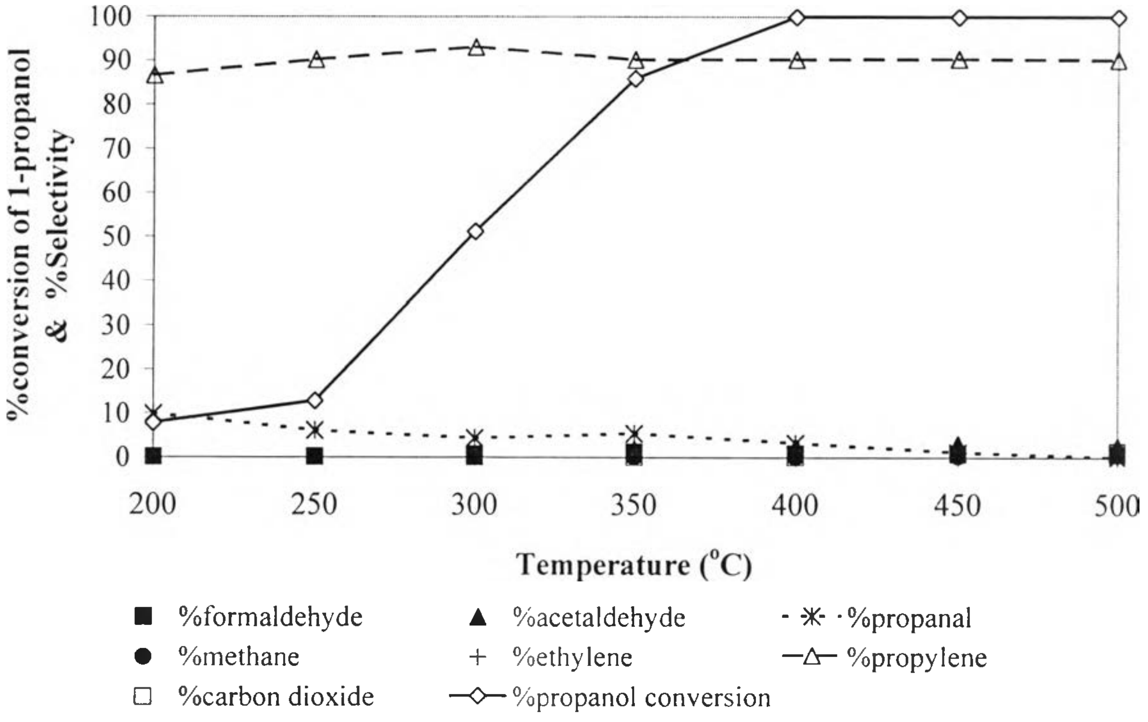

Figure 5.9b Catalytic property of co-8Co1MgAl catalyst calcined at 800°C for 7 days in the 1-propanol oxidation.

5.1.4.2 Catalytic reaction of 2-propanol

- co-8Co1MgAl calcined at 700°C for 7 days

The result of the catalytic oxidation of 2-propanol on co-8Co1MgAl catalyst calcined at 700°C for 7 days is shown in Figure 5.10a. The conversion of 2-propanol rapidly rises from 9% to 76% when the reaction temperature increases from 200 to 250 °C and slightly increases to 100% when the reaction temperature reaches 350°C. The main products of this reaction are propionaldehyde and propylene. Increasing the reaction temperature from 200 to 250 °C causes decreasing in propylene selectivity from 96% to 42%, however propionaldehyde selectivity increases from 0% to 52%.

- co-8Co1MgAl calcined at 800°C for 7 days

The behavior of co-8Co1MgAl catalyst calcined at 700°C for 7 days for 2-propanol oxidation is illustrated in Figure 5.10b. Conversion of 2-propanol rapidly rises from 1% to 100% when increases the reaction temperature from 200 to 350 °C. Propylene is main product of this reaction, its selectivity is ca. 93%.

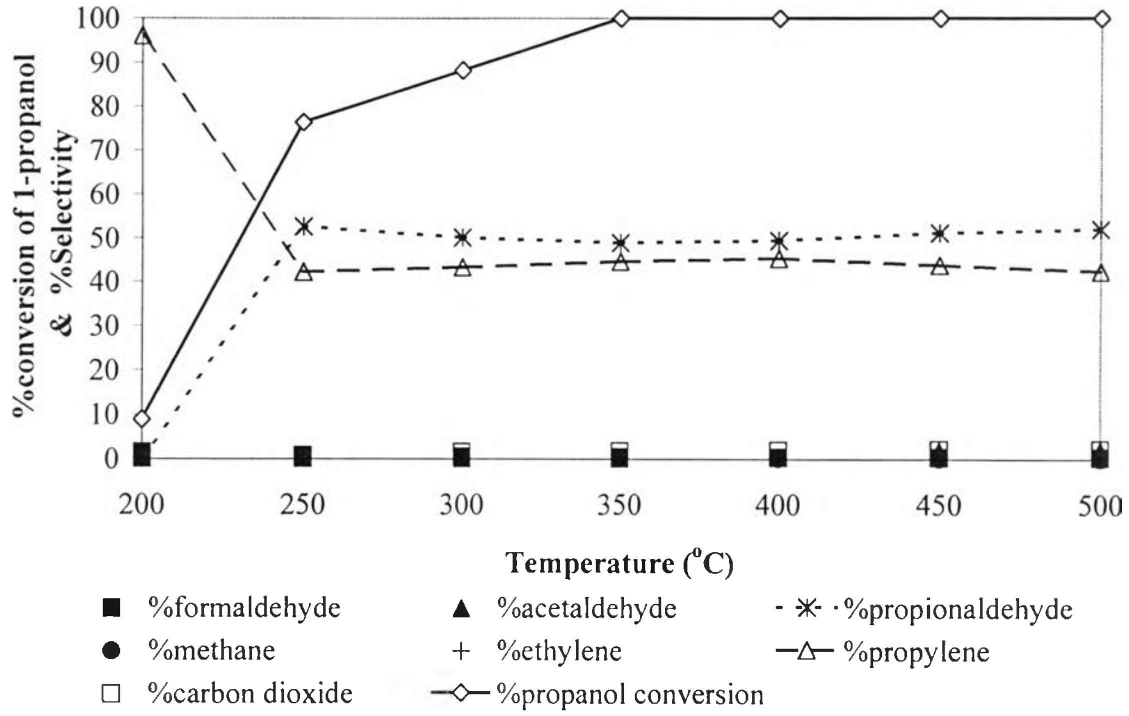

Figure 5.10a Catalytic property of co-8Co1MgAl catalyst calcined at 700°C for 7 days in the 2-propanol oxidation.

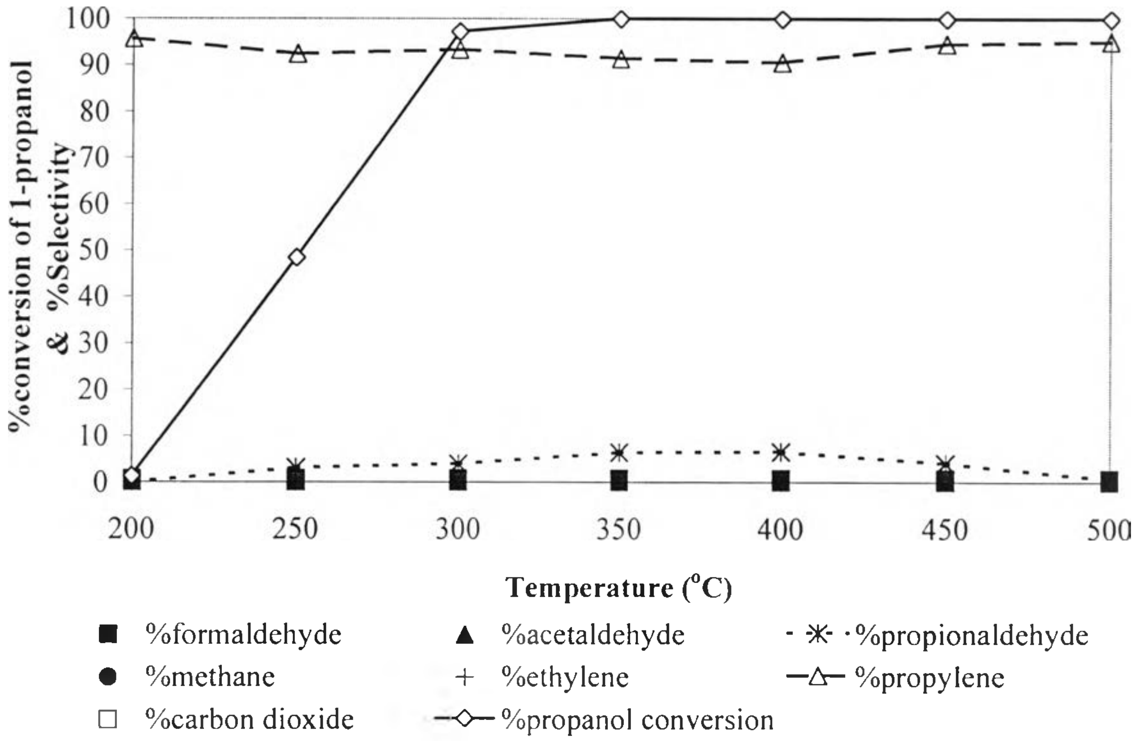

Figure 5.10b Catalytic property of co-8Co1MgAl catalyst calcined at 800°C for 7 days in the 2-propanol oxidation.

5.2 Catalyst characterization

5.2.1 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 Table 5.1.

Table 5.1 Composition of fresh catalysts.

Catalyst	%Cobalt content	%Magnesium content
8Co1MgTi	7.9	1.0
1Mg8CoTi	8.8	0.83
co-8Co1MgTi	8.6	1.0
8Co1MgAl	7.1	0.91
1Mg8CoAl	7.9	0.81
co-8Co1MgAl	8.1	0.68

Table 5.2 compares BET surface area between fresh and used catalysts over 1-propanol and 2-propanol reaction at 300 and 500 °C for 48 h. Furthermore, this table shows BET surface area of co-8Co1MgAl which are calcined at 700 and 800 °C for 7 days.

The data in Table 5.2 show that surface areas of the catalysts, 8Co1MgTi, 1Mg8CoTi, co-8Co1MgTi, 8Co1MgAl, 1Mg8CoAl, and co-8Co1MgAl which prepares in different order metal loading, are quite the same. Therefore, the sequence of cobalt and magnesium loading seem to have no effect on the surface area.

Table 5.2 BET surface area of fresh and used catalysts.

Catalyst	Fresh catalyst BET surface area (m^2/g)	Used catalyst BET surface area (m^2/g)			
		1-Propanol Reaction		2-Propanol Reaction	
		At 300°C	At 500°C	At 300°C	At 500°C
8Co1MgTi	21.02	16.09	21.72	23.17	26.57
1Mg8CoTi	24.01	27.07	65.46	23.79	67.92
co-8Co1MgTi	24.94	33.40	N.A.	24.14	41.49
8Co1MgAl	143.38	145.62	64.68	150.50	136.94
1Mg8CoAl	133.35	126.49	90.56	144.83	124.56
co-8Co1MgAl	124.18	128.14	N.A.	119.49	109.66
co-8Co1MgAl [1]	140.81	-	-	-	-
co-8Co1MgAl [2]	134.52	-	-	-	-

Note: 1 calcined at 700°C for 7 days

2 calcined at 800°C for 7 days

N.A. Not available

From Table 5.2, surface areas of used 8Co1MgTi catalysts show only little difference from fresh catalyst. In case of 1Mg8CoTi, surface area of used catalysts in 1-propanol and 2-propanol oxidation at 500°C for 48 h extremely increase from fresh catalyst whereas 1Mg8CoTi used catalysts on 1-propanol and 2-propanol oxidation reaction at 300°C do not show important deviation. Surface areas of used co-8Co1MgTi catalysts in 1-propanol and 2-propanol at 500°C show little higher than fresh co-8Co1MgTi catalyst. Used 8Co1MgAl catalyst surface areas in 1-propanol at 300°C and 2-propanol at 300 and 500°C are very close to fresh 8Co1MgAl catalyst surface area. Surface area of the used 1Mg8CoAl catalysts decrease when compare with the fresh catalyst except the used 1Mg8CoAl catalyst in 2-propanol reaction at 300°C, its surface area increases from 133.35 m^2/g to 144.83 m^2/g. For co-8Co1MgAl catalyst, the used catalysts in the oxidation of 1-propanol at 300°C, 2-propanol at 300 and 500°C surface area are 128.14, 119.49 and 109.66 m^2/g respectively. Surface area of co-8Co1MgAl catalysts calcined at 700 and 800 °C for 7 days are 140.81 and 134.52 m^2/g respectively.

The changes of the surface area are due to several causes. It is found that the used catalysts contained some deposited carbonaceous compounds. In several cases (e.g. 8Co1MgAl used catalyst on 1-propanol oxidation at 500°C and co-8Co1MgAl used catalyst on 2-propanol oxidation at 500°C), a large amount carbon compounds deposited in the bed as seen from the volume of catalyst bed after the reaction was higher than before the reaction. Although the removal of the formed carbonaceous particles from the used catalyst can be carried by burning the used catalyst in air, such method requires high temperature which can lead to the sintering of the catalyst during the burning process. Since we could not separate the catalyst particles from the formed carbonaceous particles without disturbing the catalyst, the measured BET surface areas of the used catalysts did not represent the real surface areas of the catalysts. But it is the average value between the surface area of the used catalyst and the surface area of the formed carbonaceous particles.

5.2.2 X-ray Diffraction (XRD)

The crystal structures of the catalysts were identified by X-ray diffraction technique. Figures 5.11-5.12 illustrated XRD spectra of fresh catalysts (TiO_2, 8Co1MgTi, 1Mg8CoTi, co-8Co1MgTi, Al_2O_3, 8Co1MgAl, 1Mg8CoAl, and co-8Co1MgAl) and Figures 5.13-5.16 compare XRD spectra between used and each fresh catalysts.

The XRD patterns of 8Co1MgTi, 1Mg8CoTi and co-8Co1MgTi catalysts in Figure 5.11 show peaks at 2θ values that can be attributed to the support (anatase phase at 25°, 37.6°, 48°, 54°, 56° and the rutile phase at 27.3°, 36°, 41°, 57°). Beside support peak, there is one strange peak at 32° which was studied in previous works that the XRD pattern of Co_2O_3 shows 6 peaks at 20°, 32°, 37°, 45°, 60°, and 65.5° [Jan Petryk *et al.* (2000)]. The other peaks of Co_2O_3 may not be seen because they have the same position as TiO_2. From this result, it can not conclude what structure of Co_2O_3 formed on TiO_2 surface. Cobalt oxide may form a Co_2O_3 crystal structure on the TiO_2 support or may react with MgO to form a new Co-Mg-O compound. The structure of Co-Mg-O/TiO_2 catalyst is similar to TiO_2 but more amorphous.

Figure 5.12 demonstrates that the XRD patterns of these catalysts (8Co1MgAl, 1Mg8CoAl, co-8Co1MgAl, co-8Co1MgAl calcined at 700°C for 7 days and co-8Co1MgAl calcined at 700°C for 7 days) are the same as Al_2O_3 support. The XRD pattern of Al_2O_3 catalyst shows 7 peaks at 31°, 37°, 45°, 46°, 56°, 59° and 65.5° that are the same positions as Co_2O_3 catalyst. This means that the crystalline Co_3O_4 catalyst peaks in Co-Mg-O/Al_2O_3 catalyst are not measurable because in these regions the XRD patterns of Co_3O_4 are hidden by the XRD patterns of Al_2O_3 support.

In case of the used catalysts, most of them illustrate the same pattern as fresh catalysts as can be seen from Figures 5.13-5.16 except the XRD pattern of used 8Co1MgAl catalyst on 1-propanol oxidation at 500°C and used 1Mg8CoTi catalysts on both 1-propanol and 2-propanol oxidation at 500°C which all appear the unknown peak at 26°.

Since there is no trend between the changes in the XRD spectra and the catalytic activity of the catalysts used at 300 and 500°C. We can conclude that, in the operating conditions studied, the change in the catalyst structure does not affect the catalytic activity of the catalysts.

The exception is the catalyst calcined at 800°C for 7 days (co-8Co1MgAl). The XRD spectrum of this catalyst is the same as of the fresh one. However, the catalytic property of the catalyst drastically changed. The activity of the catalyst is still high but the main reaction product, see Figures 5.9b and 5.10b, change to propylene rather than propionaldehyde. The selectivity toward propionaldehyde drops to near zero. This result suggests that there must be some change in the structure of the Co-Mg-O compound on the alumina surface. The calcination at 800° C for 7 days causes the Co-Mg-O compound changes to a new phase, which prefers the dehydration rather than the oxidation of 1-propanol and 2-propanol.

The change in product selectivity is not pronounced if the catalyst is calcined at only 700°C for 7 days. Therefore, we can estimate that the calcination temperature causing the transformation of the Co-Mg-O compound on the alumina surface should lies between 700°C and 800°C.

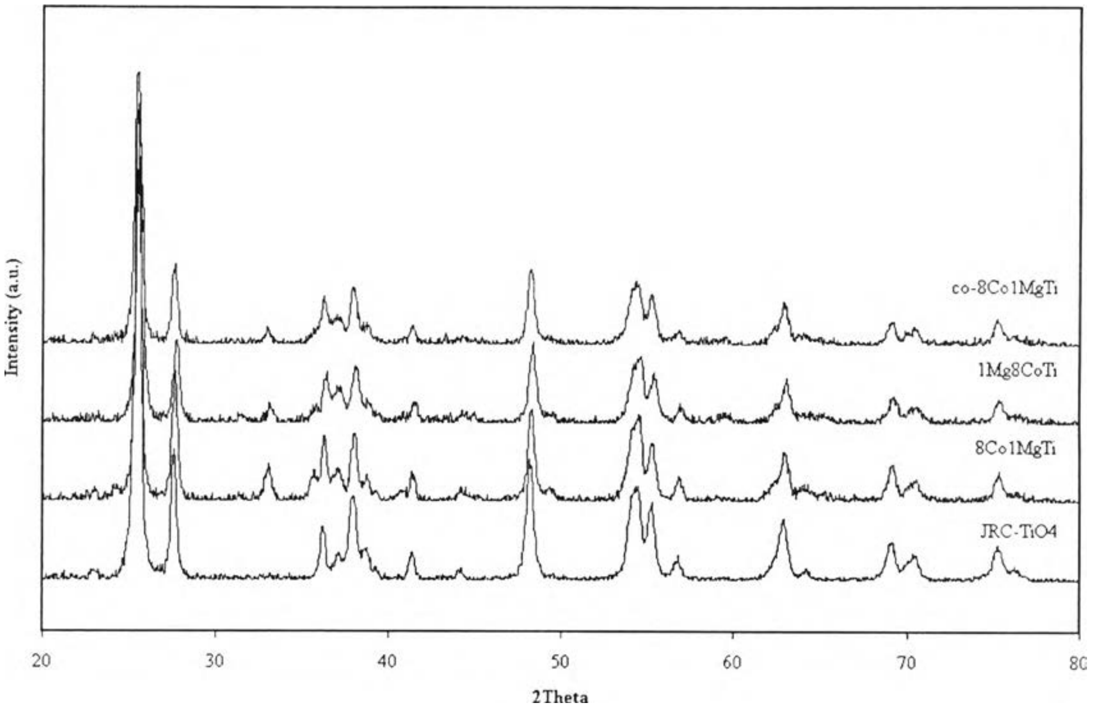

Figure 5.11 The XRD pattern of JRC-TiO4, 8Co1MgTi, 1Mg8CoTi and co-8Co1MgTi catalysts

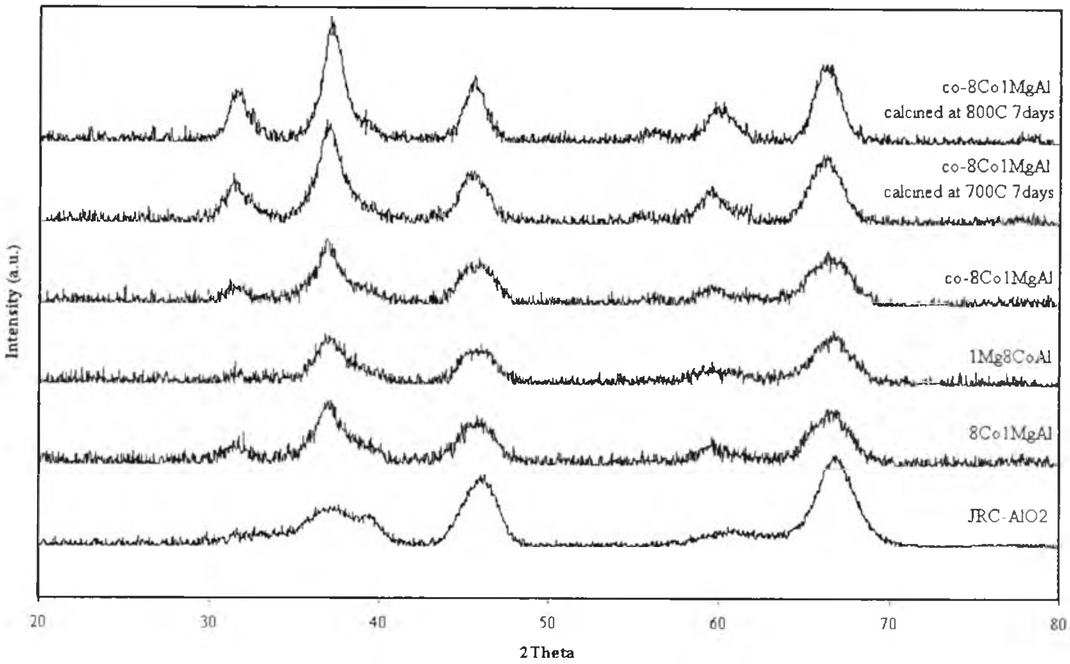

Figure 5.12 The XRD pattern of JRC-AlO2, 8Co1MgAl, 1Mg8CoAl, co-8Co1MgAl, co-8Co1MgAl calcined at 700°C for 7 days and co-8Co1MgAl calcined at 800°C for 7 days catalysts

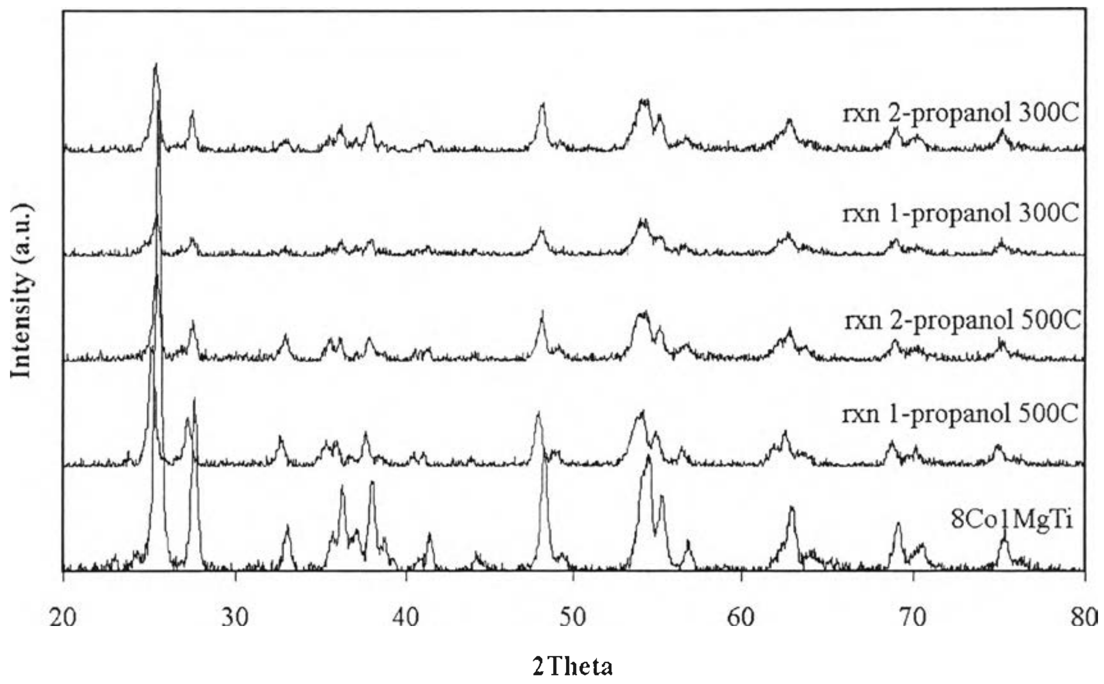

Figure 5.13 The XRD pattern of 8Co1MgTi catalyst compare with used catalysts on 1-propanol and 2-propanol reaction at 300°C and 500°C for 48h.

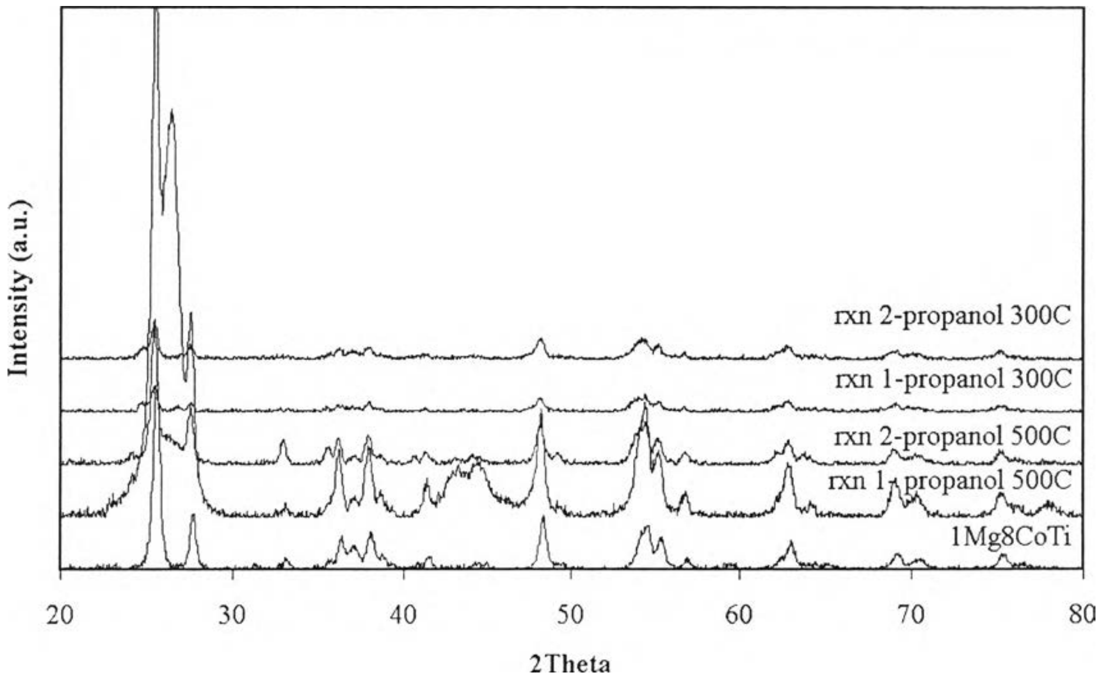

Figure 5.14 The XRD pattern of 1Mg8CoTi catalyst compare with used catalysts on 1-propanol and 2-propanol reaction at 300°C and 500°C for 48h.

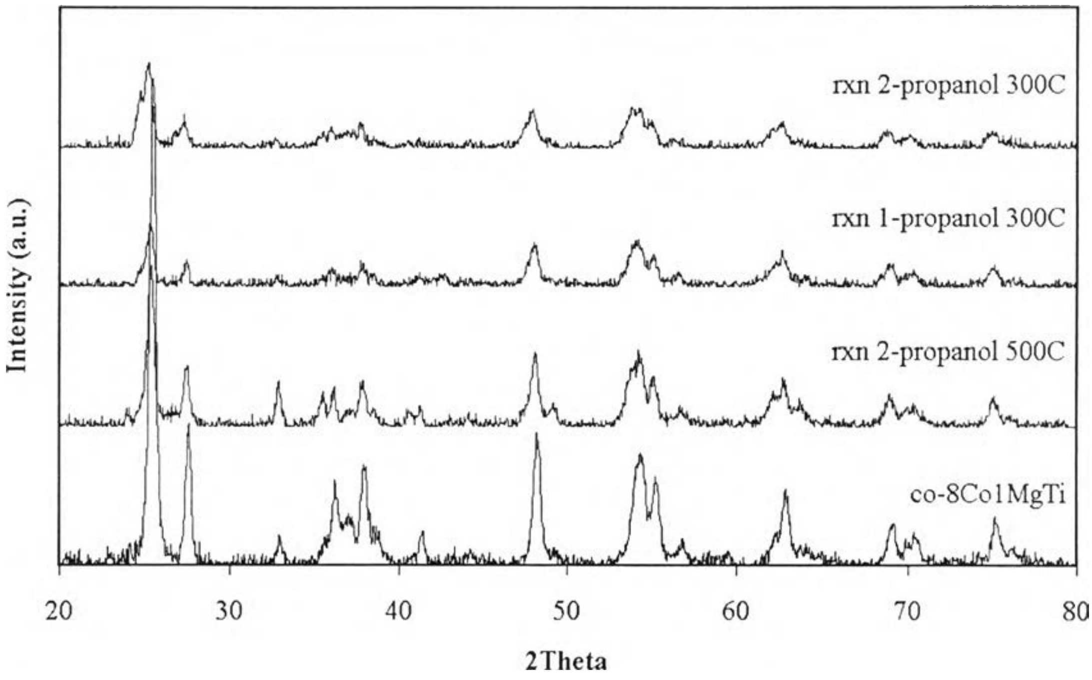

Figure 5.15 The XRD pattern of co-8Co1MgTi catalyst compare with used catalysts on 1-propanol and 2-propanol reaction at 300°C and 500°C for 48h.

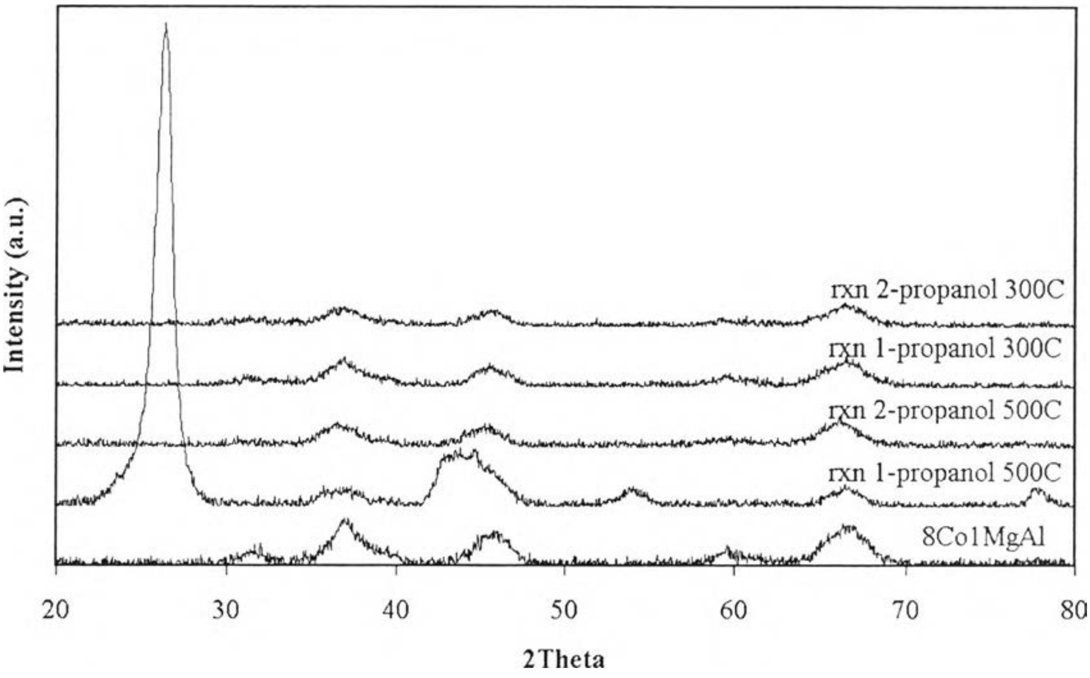

Figure 5.16 The XRD pattern of 8Co1MgAl catalyst compare with used catalysts on 1-propanol and 2-propanol reaction at 300°C and 500°C for 48h.

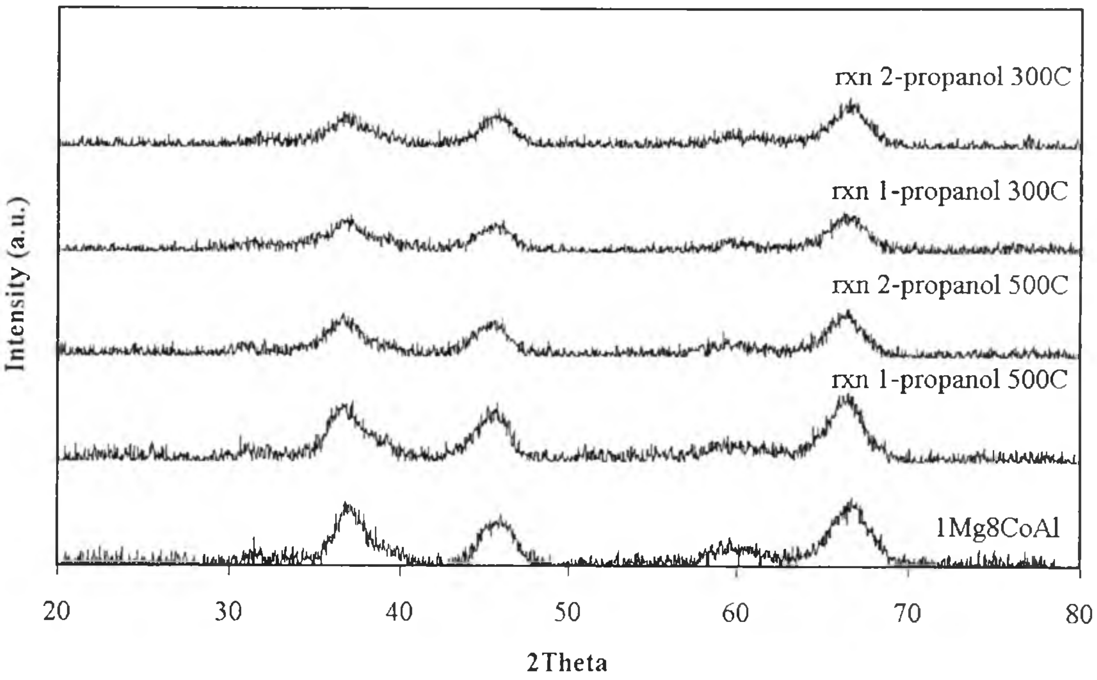

Figure 5.17 The XRD pattern of 1Mg8CoAl catalyst compare with used catalysts on 1-propanol and 2-propanol reaction at 300°C and 500°C for 48h.

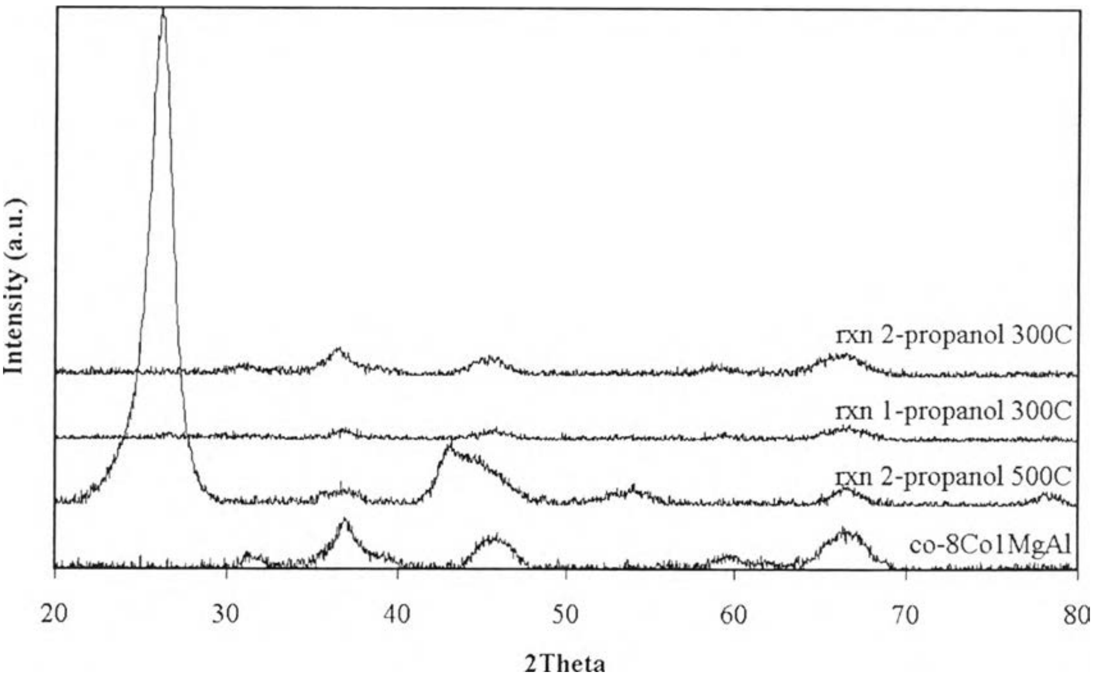

Figure 5.18 The XRD pattern of co-8Co1MgAl catalyst compare with used catalysts on 1-propanol and 2-propanol reaction at 300°C and 500°C for 48h.

5.2.3 Temperature programmed oxidation (TPO)

The amounts of carbon deposited on the spent catalysts are characterized employing the TPO technique. Carbon deposited quantity computed from the area underneath the TPO curve is described in Table 5.3

The TPO profiles observed over the used catalysts are illustrated in Figures 5.19a-5.24c. From temperature programmed oxidation result, it was found that the used catalysts in the oxidation reaction at 500°C for 48h. have more amounts of carbon deposited than the used catalysts on oxidation at 300°C.

The TPO result shows that the amounts of coke deposited on the catalyst must relate to the activity of the catalyst. In the case where a large amount of carbon is found, the reactant conversion shows a significant drop during the on stream period. Examples of such case are 1Mg8CoTi in 1-propanol and 2-propanol oxidation at 500° C, 8Co1MgAl in 1-propanol and 2-propanol oxidation at 500°C, 1Mg8CoAl in 1-propanol and 2-propanol oxidation at 500°C and co-8Co1MgAl in 2-propanol oxidation at 500°C. The coke deactivates the catalyst by blocking the active sites on the catalyst surface preventing the reactant to reach the active sites. It is interesting to find that the amount of coke formed at 500°C is much higher than at 300°C. This fact suggests that a high enough reaction temperature is required to form a coke precursor species.

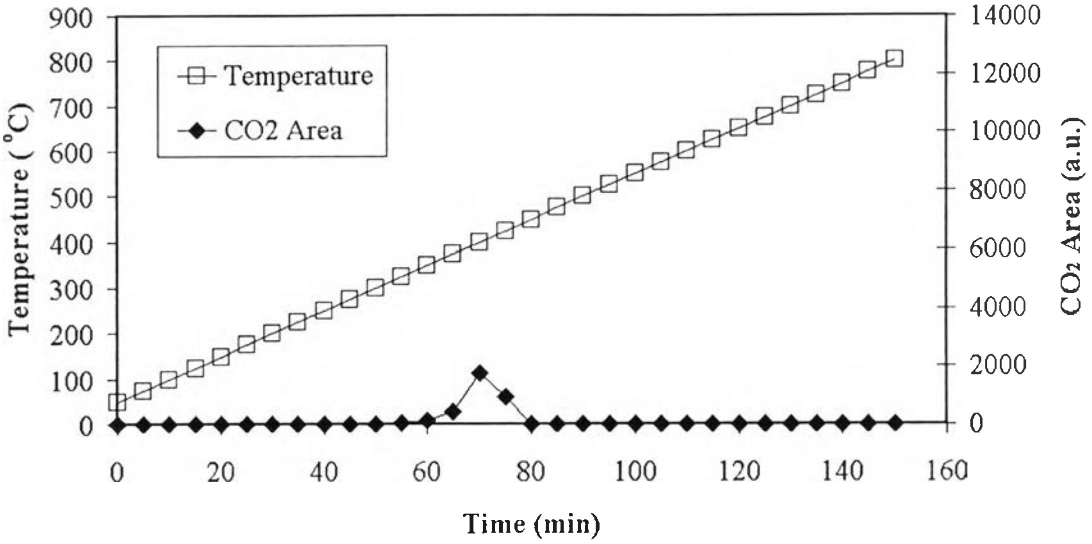

Figure 5.19a Temperature programmed oxidation of used 8Co1MgTi catalyst on 1-propanol reaction at 300°C for 48h.

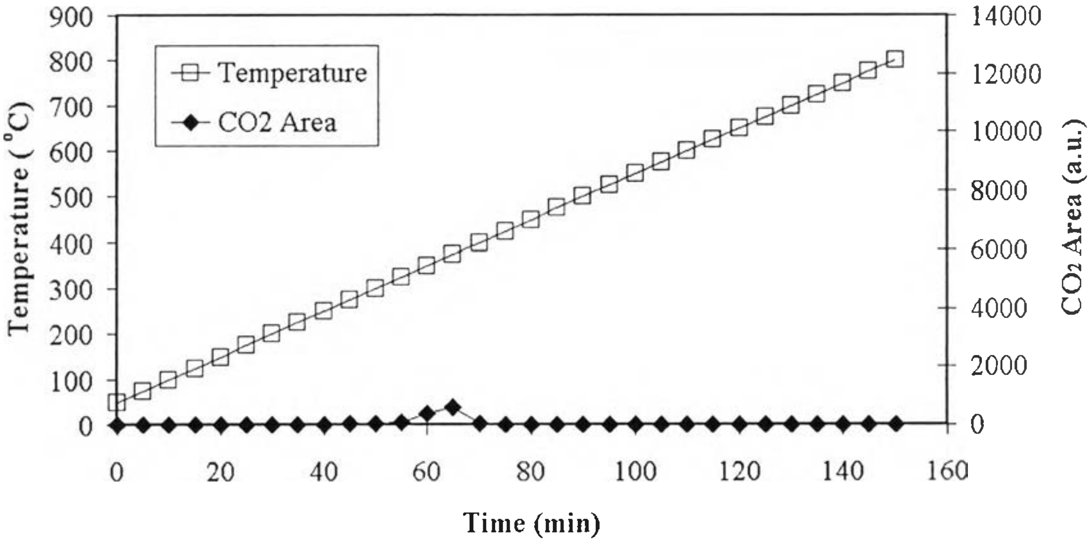

Figure 5.19b Temperature programmed oxidation of used 8Co1MgTi catalyst on 2-propanol reaction at 300°C for 48h.

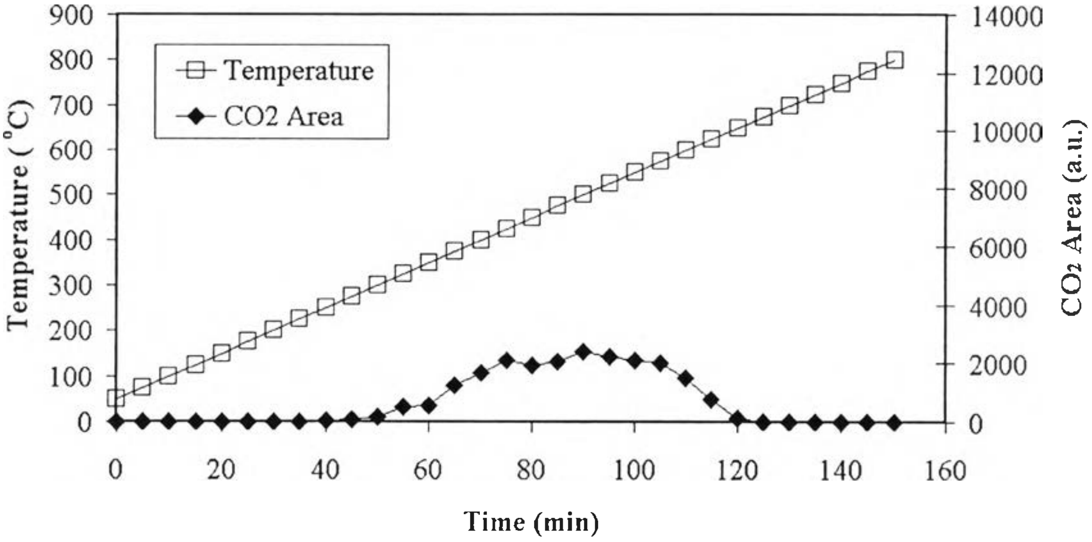

Figure 5.19c Temperature programmed oxidation of used 8Co1MgTi catalyst on 1-propanol reaction at 500°C for 48h.

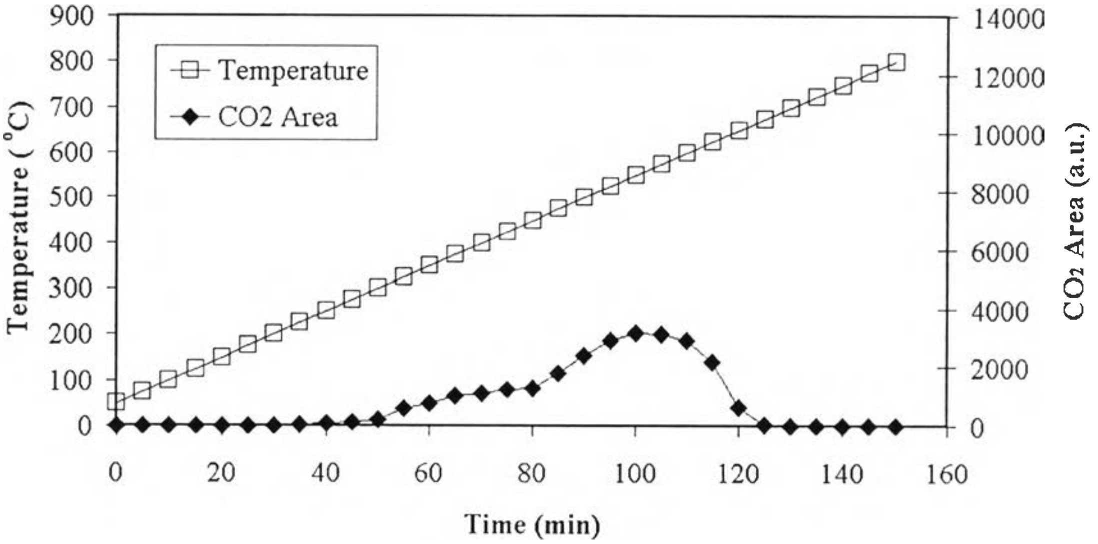

Figure 5.19d Temperature programmed oxidation of used 8Co1MgTi catalyst on 2-propanol reaction at 500°C for 48h.

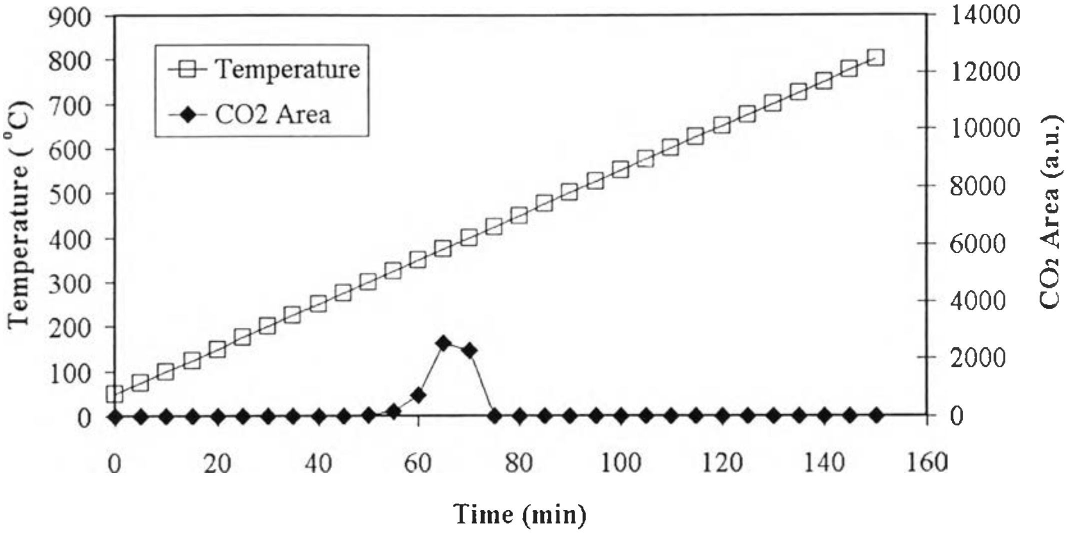

Figure 5.20a Temperature programmed oxidation of used 1Mg8CoTi catalyst on 1-propanol reaction at 300°C for 48h.

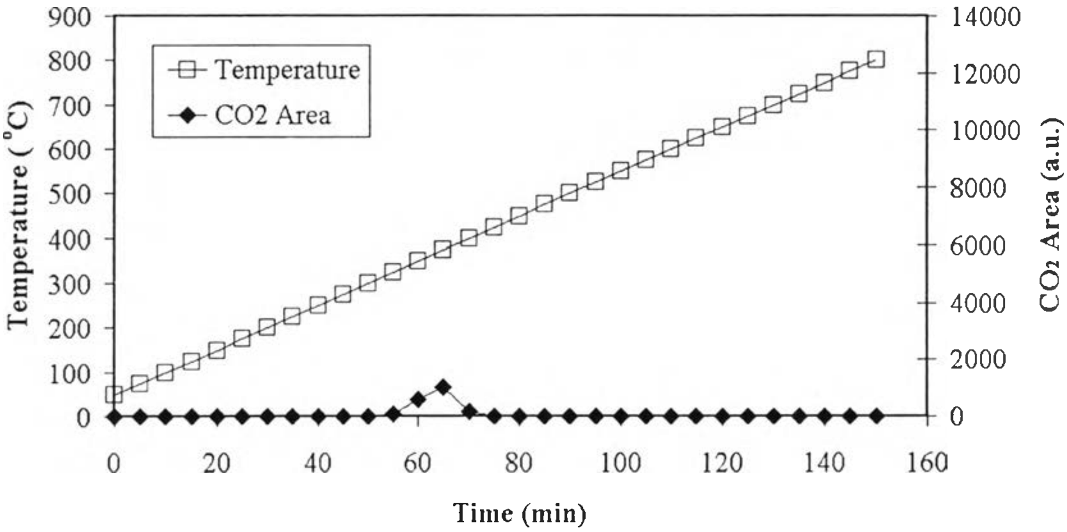

Figure 5.20b Temperature programmed oxidation of used 1Mg8CoTi catalyst on 2-propanol reaction at 300°C for 48h.

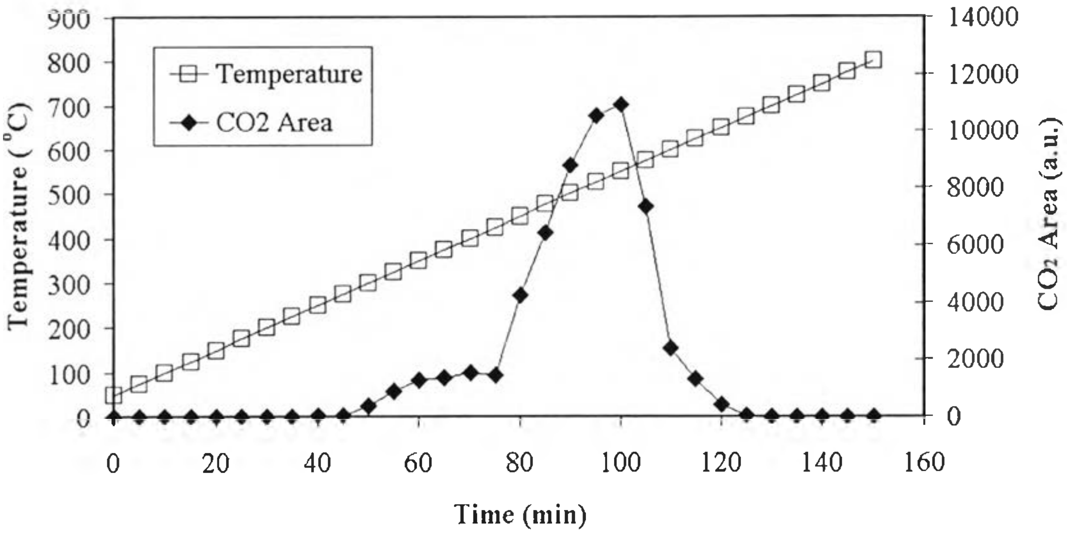

Figure 5.20c Temperature programmed oxidation of used 1Mg8CoTi catalyst on 1-propanol reaction at 500°C for 48h.

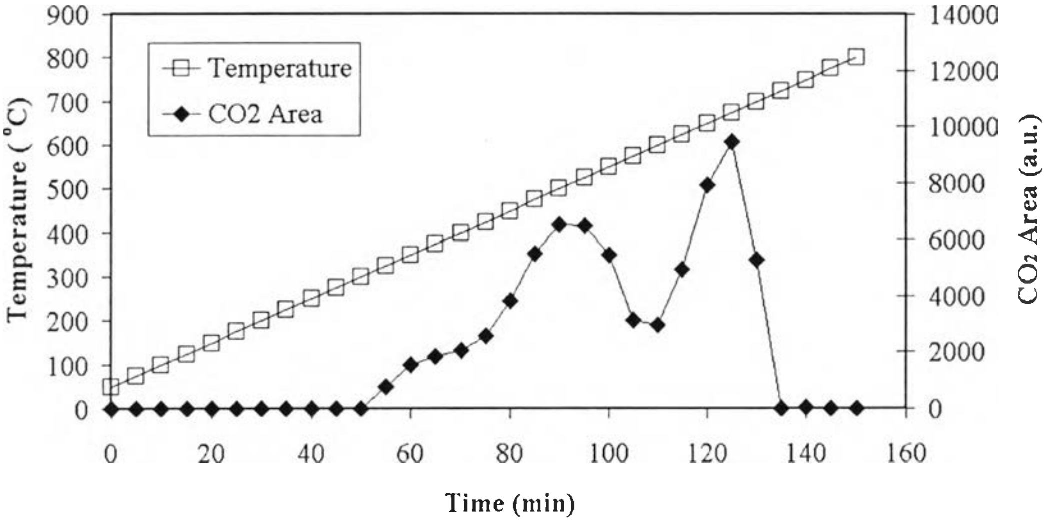

Figure 5.20d Temperature programmed oxidation of used 1Mg8CoTi catalyst on 2-propanol reaction at 500°C for 48h.

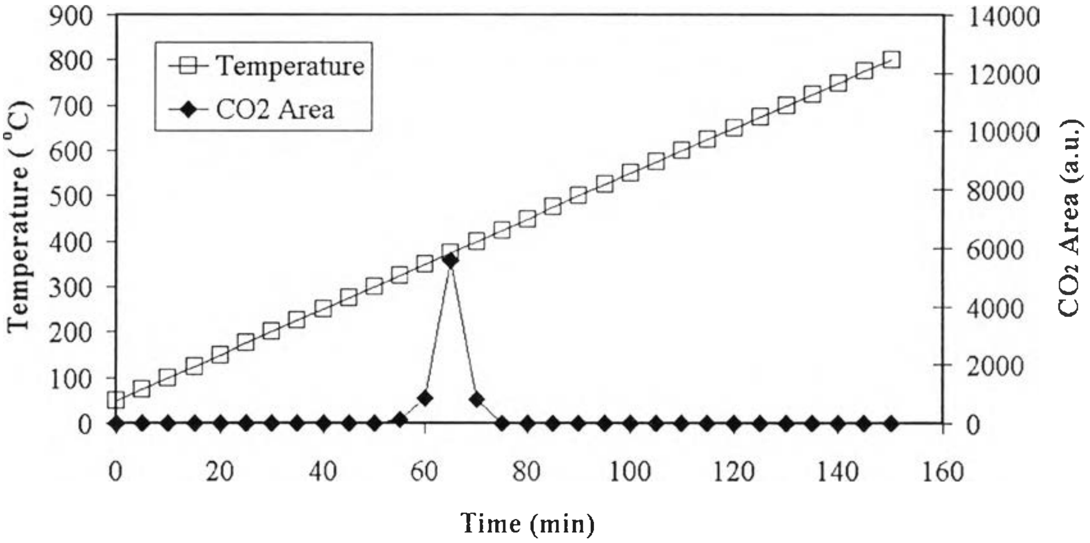

Figure 5.21a Temperature programmed oxidation of used co-8Co1MgTi catalyst on 1-propanol reaction at 300°C for 48h.

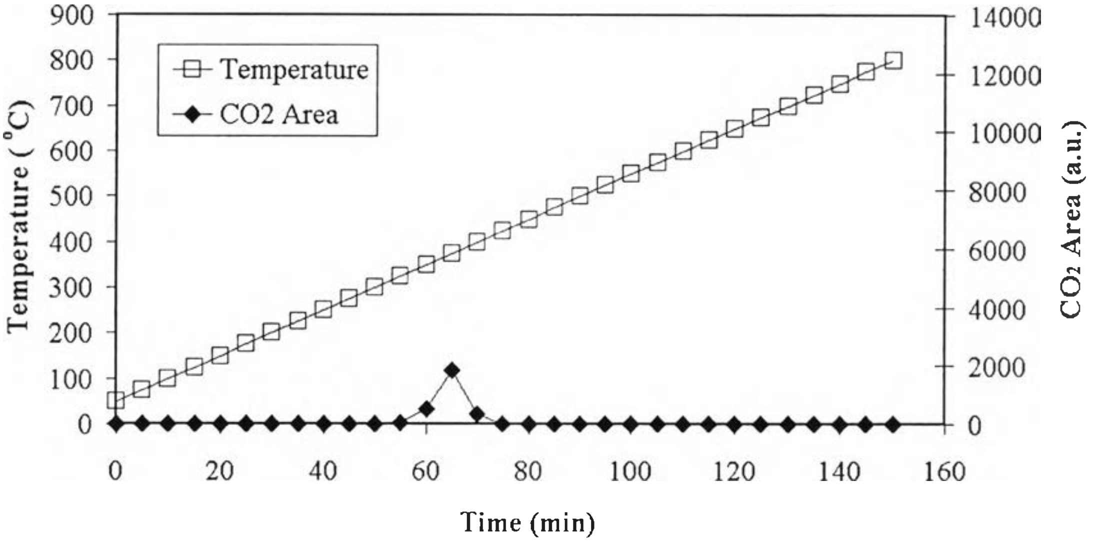

Figure 5.21b Temperature programmed oxidation of used co-8Co1MgTi catalyst on 2-propanol reaction at 300°C for 48h.

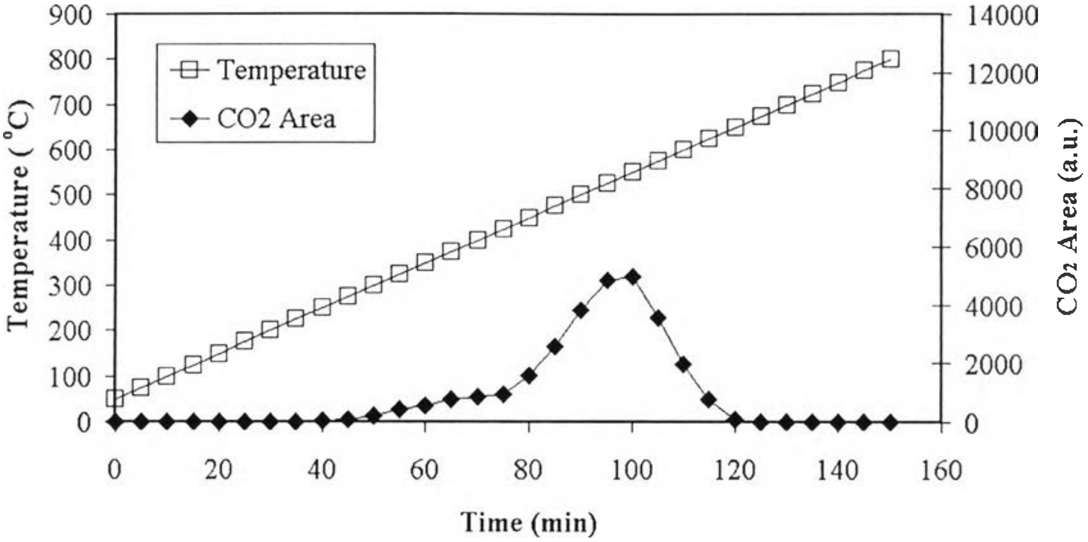

Figure 5.21c Temperature programmed oxidation of used co-8Co1MgTi catalyst on 2-propanol reaction at 500°C for 48h.

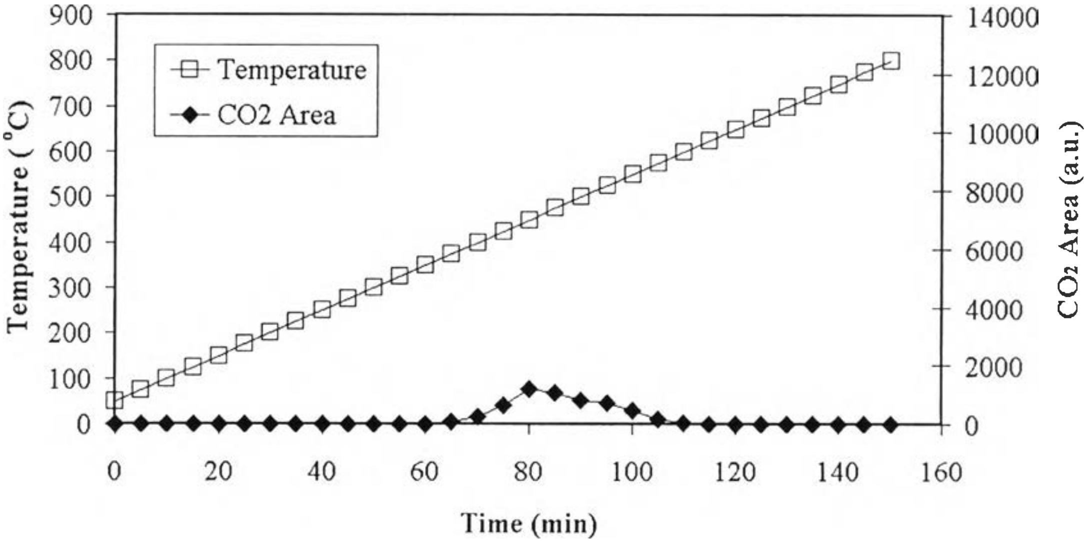

Figure 5.22a Temperature programmed oxidation of 8Co1MgAl used catalyst on 1-propanol reaction at 300°C for 48h.

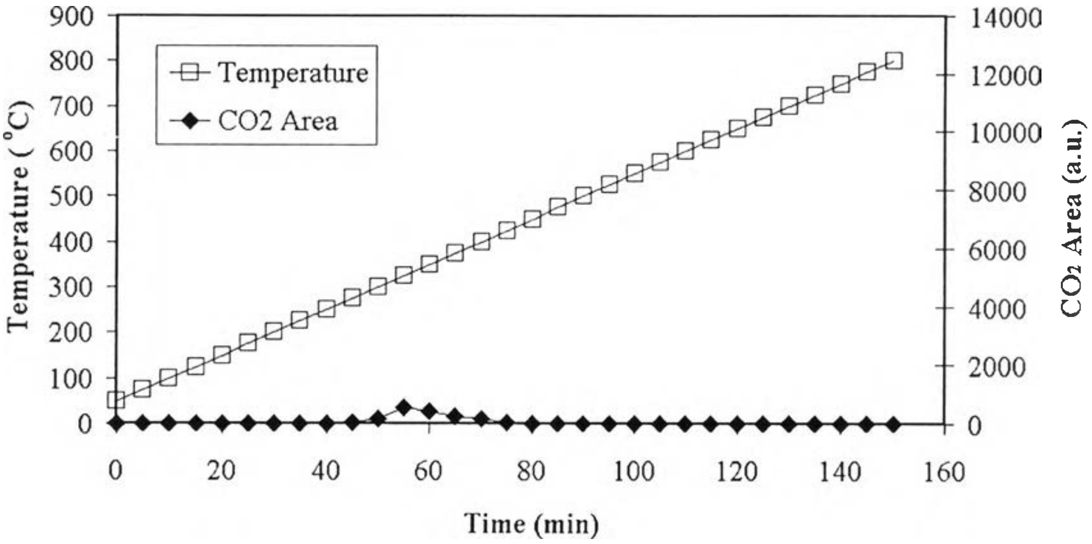

Figure 5.22b Temperature programmed oxidation of 8Co1MgAl used catalyst on 2-propanol reaction at 300°C for 48h.

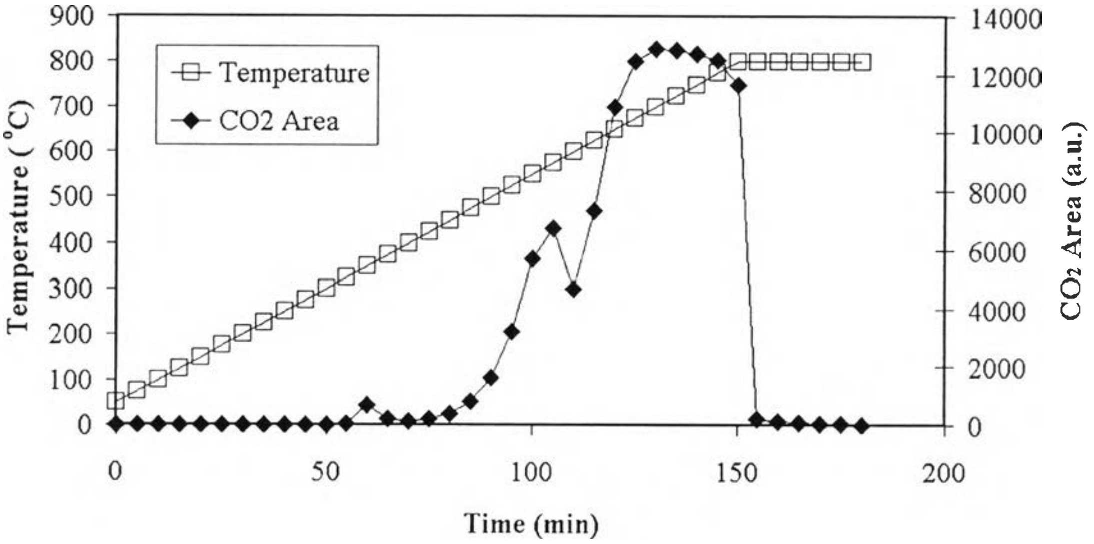

Figure 5.22c Temperature programmed oxidation of 8Co1MgAl used catalyst on 1-propanol reaction at 500°C for 48h.

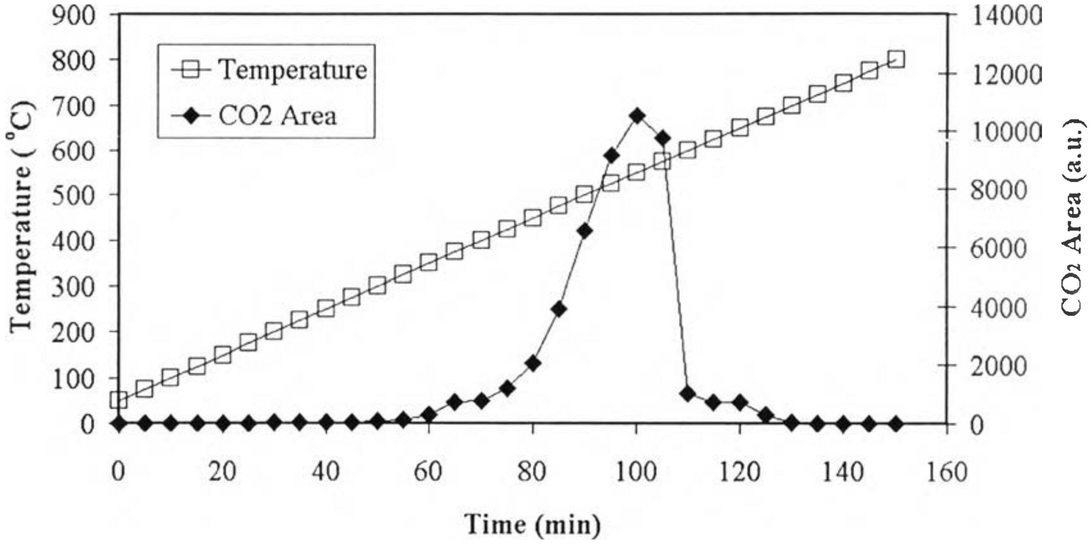

Figure 5.22d Temperature programmed oxidation of 8Co1MgAl used catalyst on 2-propanol reaction at 500°C for 48h.

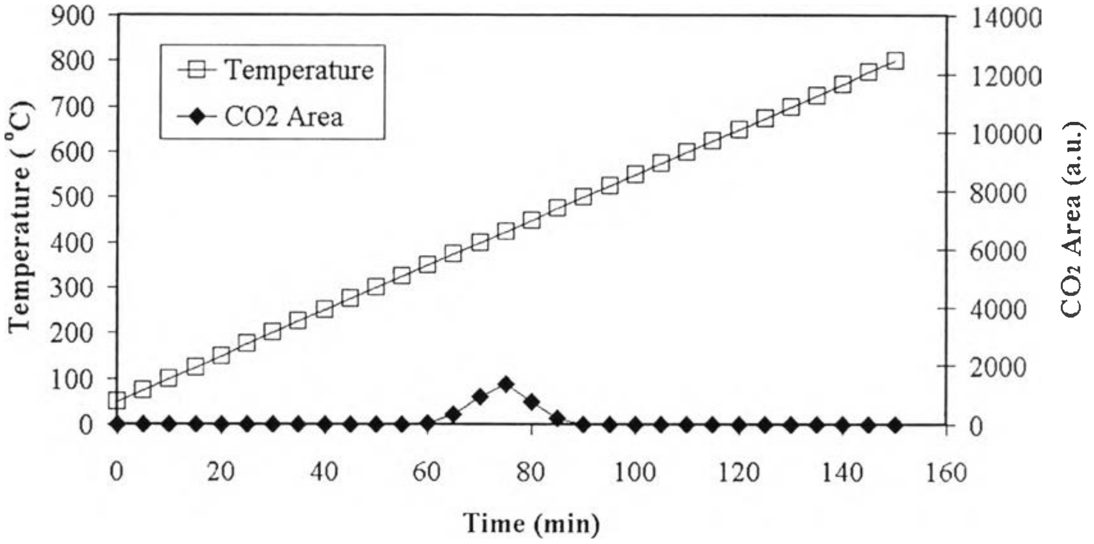

Figure 5.23a Temperature programmed oxidation of 1Mg8CoAl used catalyst on 1-propanol reaction at 300°C for 48h.

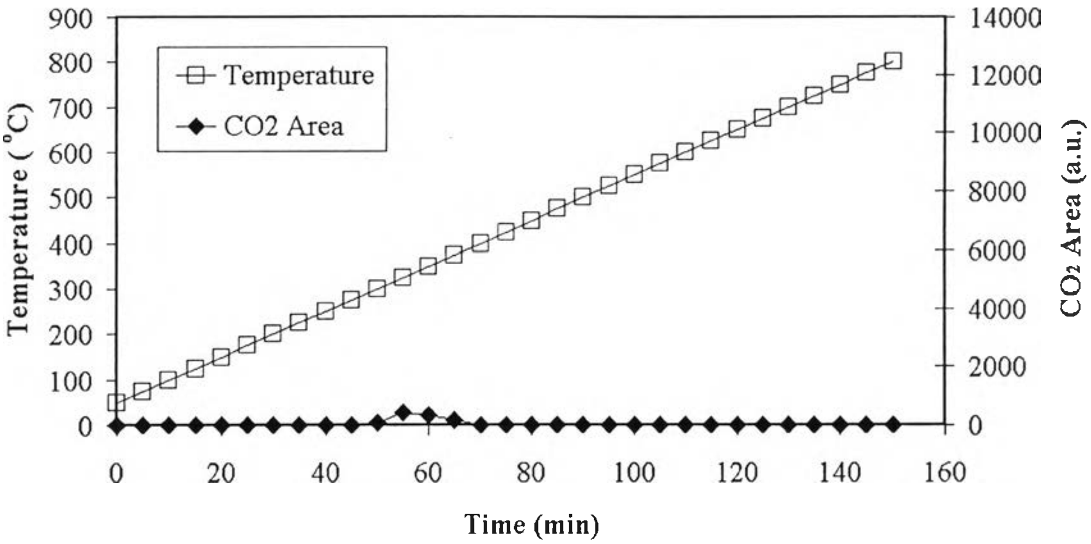

Figure 5.23b Temperature programmed oxidation of 1Mg8CoAl used catalyst on 2-propanol reaction at 300°C for 48h.

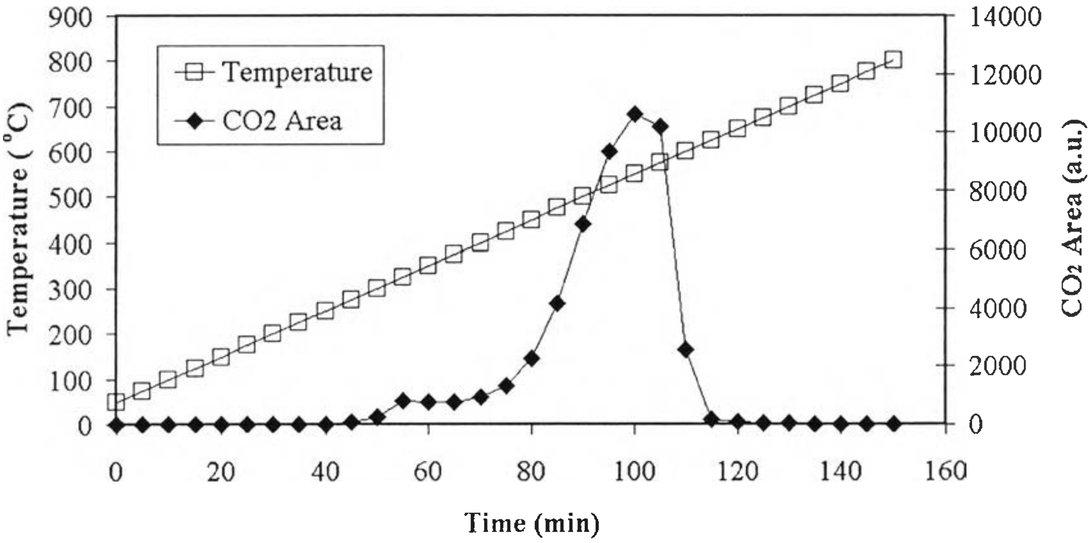

Figure 5.23c Temperature programmed oxidation of 1Mg8CoAl used catalyst on 1-propanol reaction at 500°C for 48h.

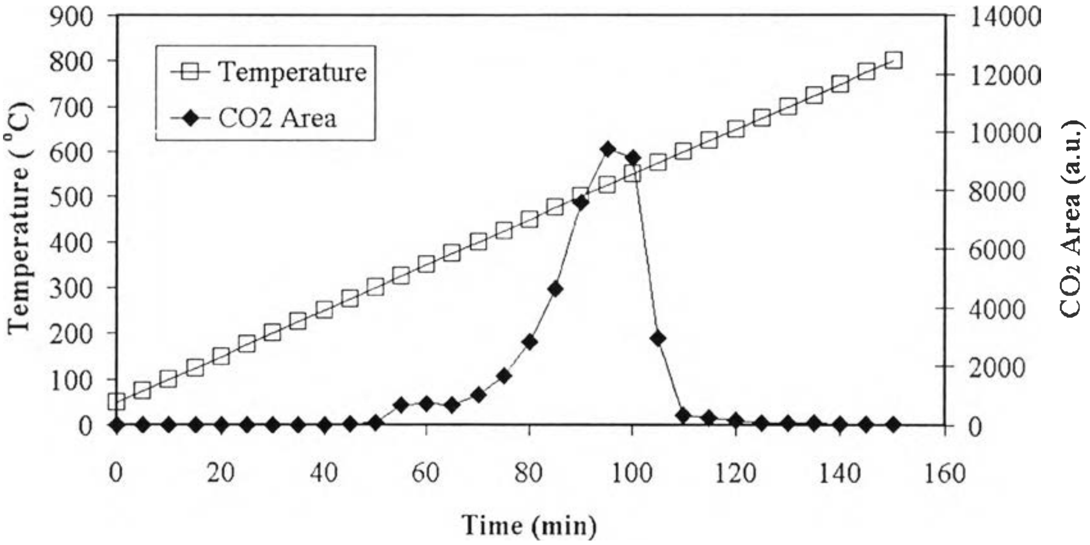

Figure 5.23d Temperature programmed oxidation of 1Mg8CoAl used catalyst on 2-propanol reaction at 500°C for 48h.

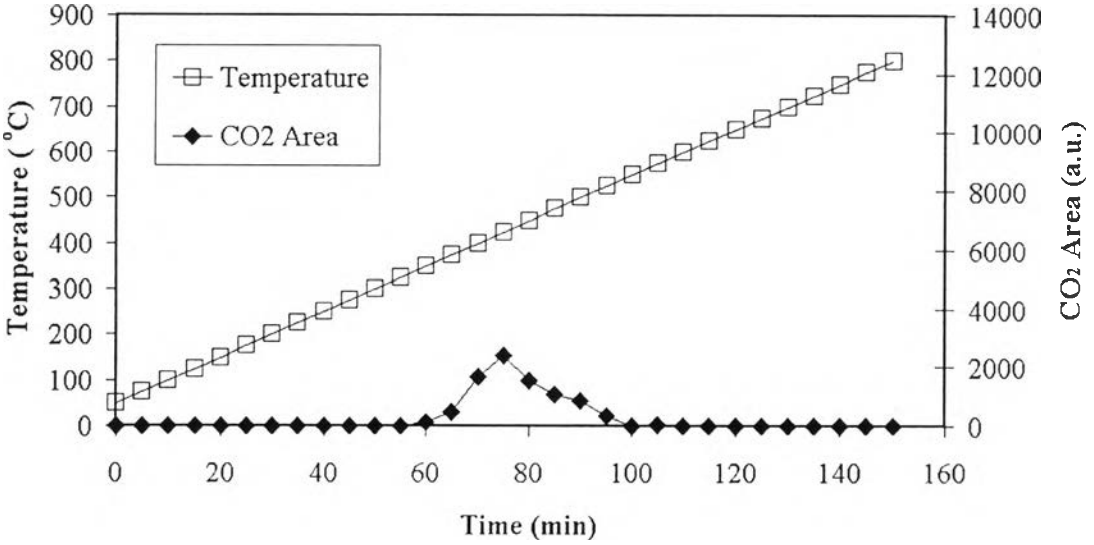

Figure 5.24a Temperature programmed oxidation of co-8Co1MgAl used catalyst on 1-propanol reaction at 300°C for 48h.

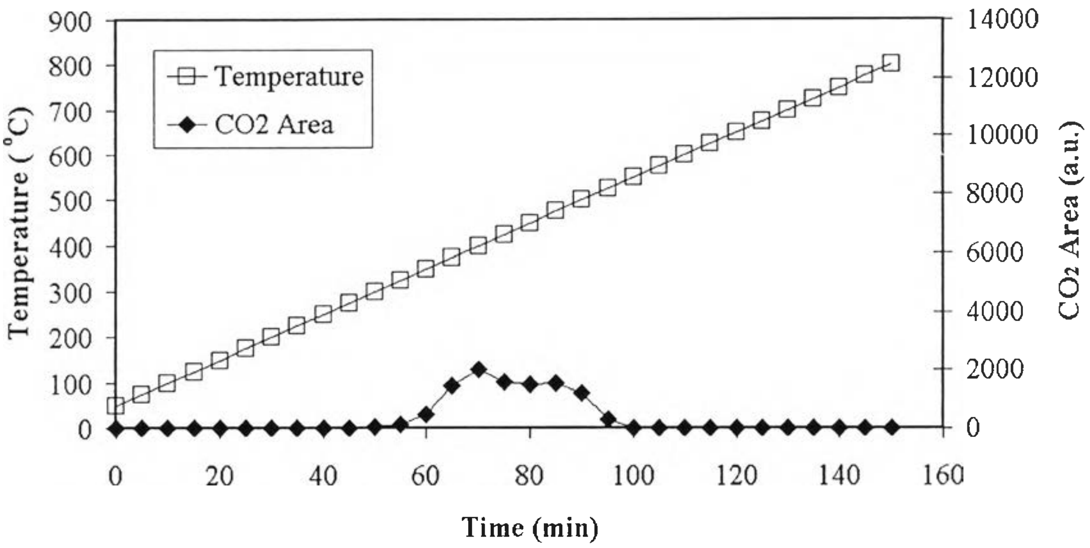

Figure 5.24b Temperature programmed oxidation of co-8Co1MgAl used catalyst on 2-propanol reaction at 300°C for 48h.

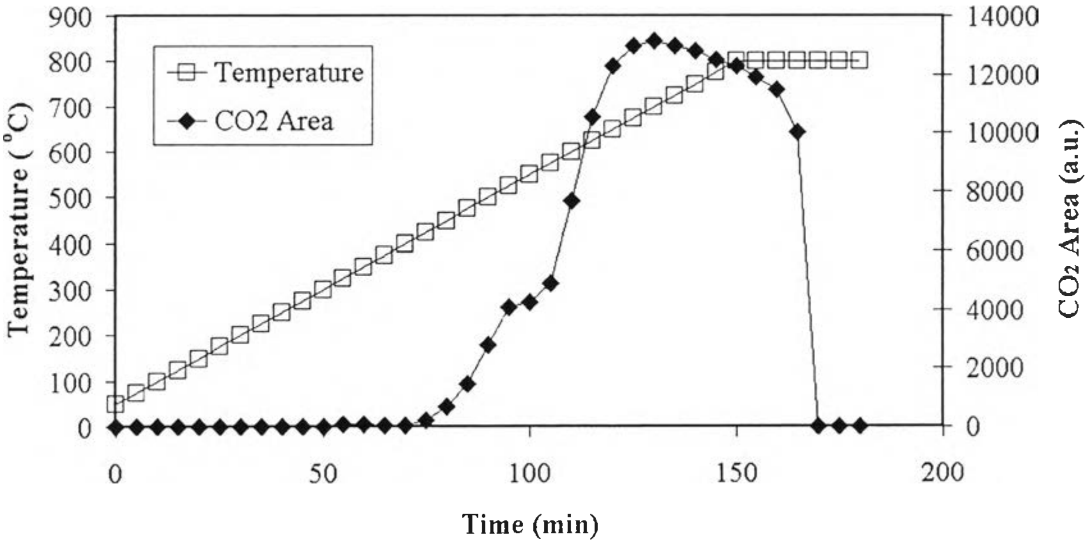

Figure 5.24c Temperature programmed oxidation of co-8Co1MgAl used catalyst on 2-propanol reaction at 500°C for 48h.

Table 5.3 Carbon percentage in used catalyst.

Catalyst	% Carbon per gram catalyst
8Co1MgTi in 1-propanol oxidation at 300°C	1.90
8Co1MgTi in 2-propanol oxidation at 300°C	0.69
8Co1MgTi in 1-propanol oxidation at 500°C	12.35
8Co1MgTi in 2-propanol oxidation at 500°C	14.74
1Mg8CoTi in 1-propanol oxidation at 300°C	3.28
1Mg8CoTi in 2-propanol oxidation at 300°C	1.10
1Mg8CoTi in 1-propanol oxidation at 500°C	34.12
1Mg8CoTi in 2-propanol oxidation at 500°C	40.30
co-8Co1MgTi in 1-propanol oxidation at 300°C	4.23
co-8Co1MgTi in 2-propanol oxidation at 300°C	1.58
co-8Co1MgTi in 2-propanol oxidation at 500°C	16.11
8Co1MgAl in 1-propanol oxidation at 300°C	3.18
8Co1MgAl in 2-propanol oxidation at 300°C	0.96
8Co1MgAl in 1-propanol oxidation at 500°C	67.90
8Co1MgAl in 2-propanol oxidation at 500°C	27.63
1Mg8CoAl in 1-propanol oxidation at 300°C	2.11
1Mg8CoAl in 2-propanol oxidation at 300°C	0.60
1Mg8CoAl in 1-propanol oxidation at 500°C	29.41
1Mg8CoAl in 2-propanol oxidation at 500°C	24.46
co-8Co1MgAl in 1-propanol oxidation at 300°C	4.93
co-8Co1MgAl in 2-propanol oxidation at 300°C	5.91
co-8Co1MgAl in 2-propanol oxidation at 500°C	88.48

5.2.4 Electron spin resonance (ESR)

Electronic structures of all catalysts in this experiment are characterized by the electron spin resonance spectrometer, which can detect unpaired electron number by measure the area under ESR spectra curve. Moreover ESR spectroscopy characterization use "g" value which is a constant value specify for a system or material which are measured to compare the electronic structure of each catalyst.

Figures 5.21-5.22 show ESR spectra of all fresh catalysts that have been used in this experiment. There is no signal of unpaired electron, this may be due to in appropriate condition of ESR spectrometer. Then it can be claimed that all of the catalyst structures overwhelm with Co^{3+} which does not has any unpaired electron.

In order to investigate the electronic structure changing of catalyst after 48 h. of reaction, used catalysts are characterized. ESR spectra of used catalysts on 1-propanol and 2-propanol oxidation at 300 and 500 °C for 48 h. are exhibited in Figures 5.25-5.32. Unpaired electron can be detected in ESR spectra of some used catalysts such as co-8Co1MgTi used in 1-propanol and 2-propanol oxidation at 300° C. They have same *g* value, which are 1.888.

Though some used catalysts show the presence of some unpaired electron, the positions of the g-value are not the same as that of Co^{2+} reported in literature, which the *g* value equal to 5.6910 [Youngwanishsate (1998)]. Therefore, we cannot confirm that the found unpaired electron belong to Co^{2+} species. In the same way, *g* value for carbon radicals is 2.003 [Srihirunpullop (2000)], which is not agree with result in this experiment. Then it can not conclude that unpaired electron, which is detected, belong to carbon deposited on the catalysts.

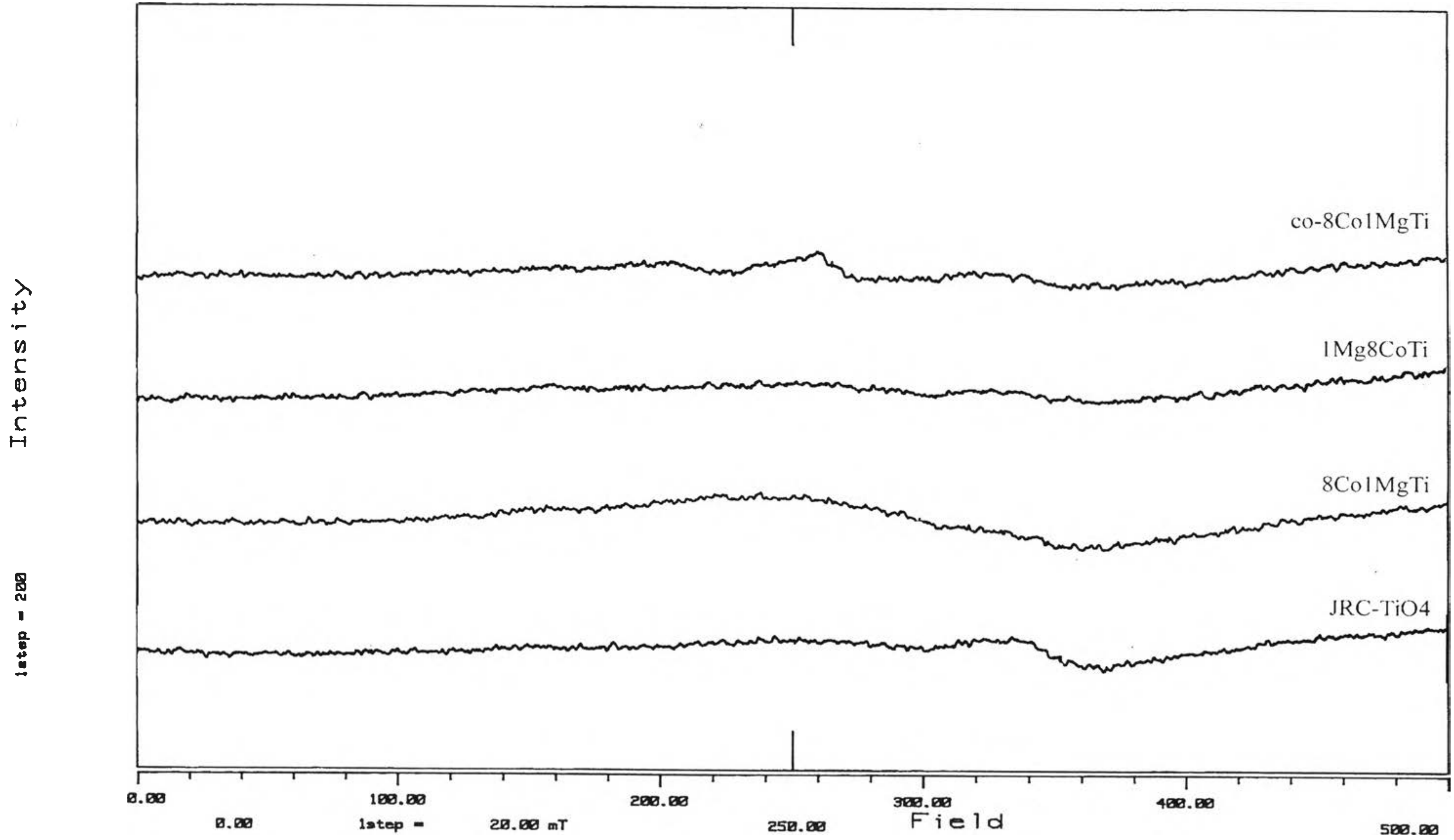

Figure 5.25 ESR spectra of JRC-TiO4, 8Co1MgTi, 1Mg8CoTi and co-8Co1MgTi

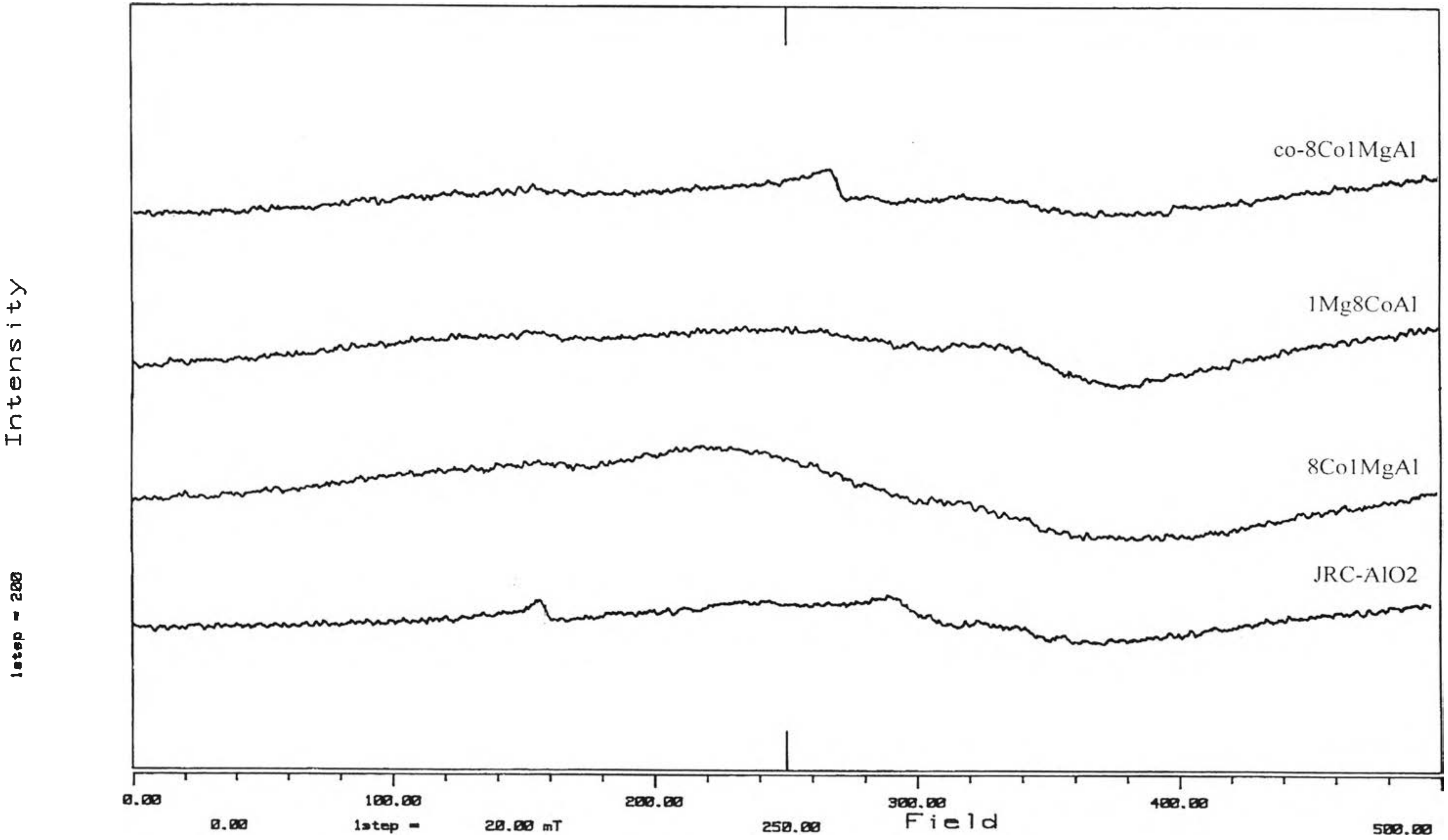

Figure 5.26 ESR spectra of JRC-AlO2, 8Co1MgAl, 1Mg8CoAl and co-8Co1MgAl

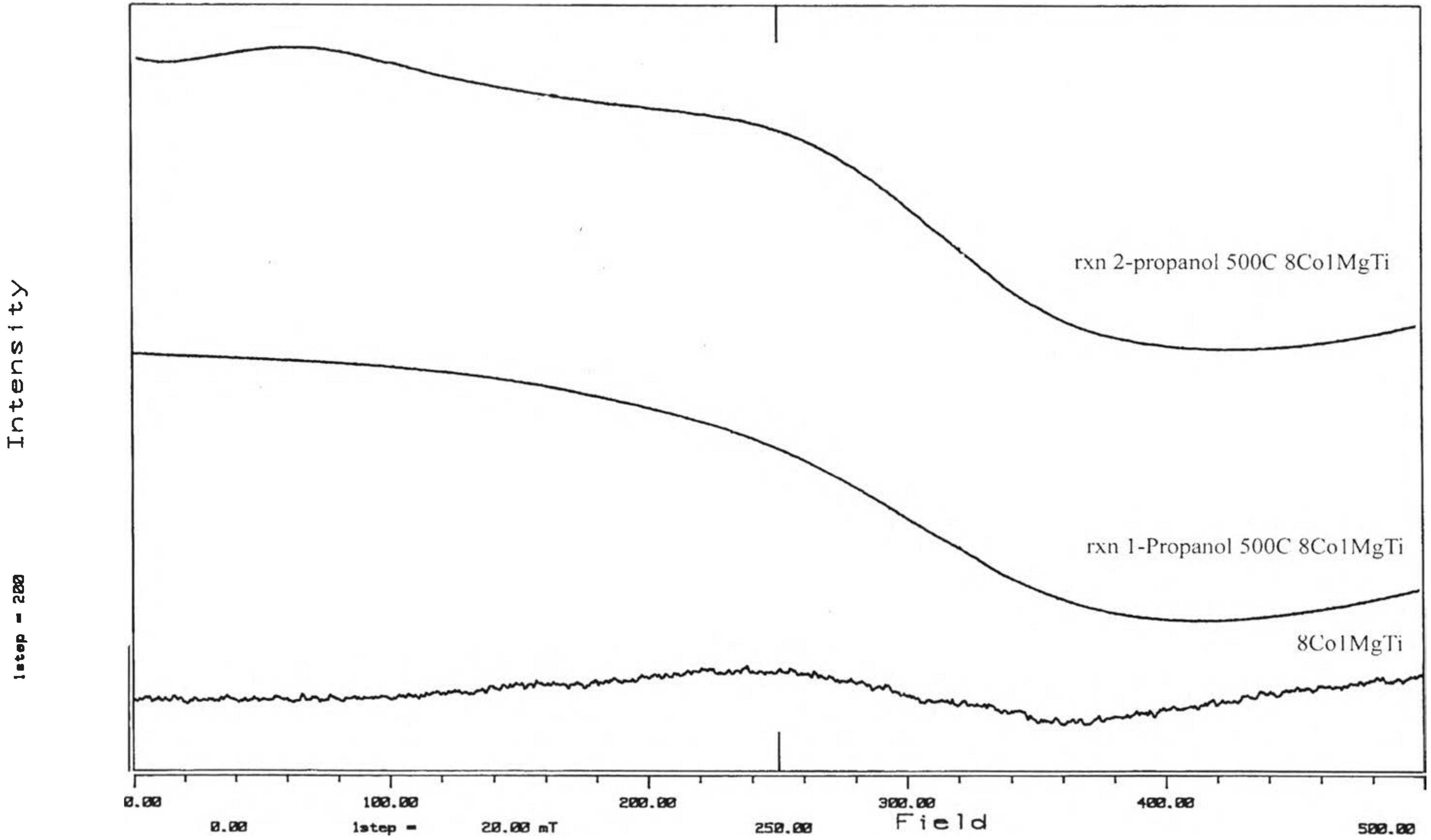

Figure 5.27 ESR spectra of used 8Co1MgTi catalysts on 1- propanol and 2-propanol at 500 °C

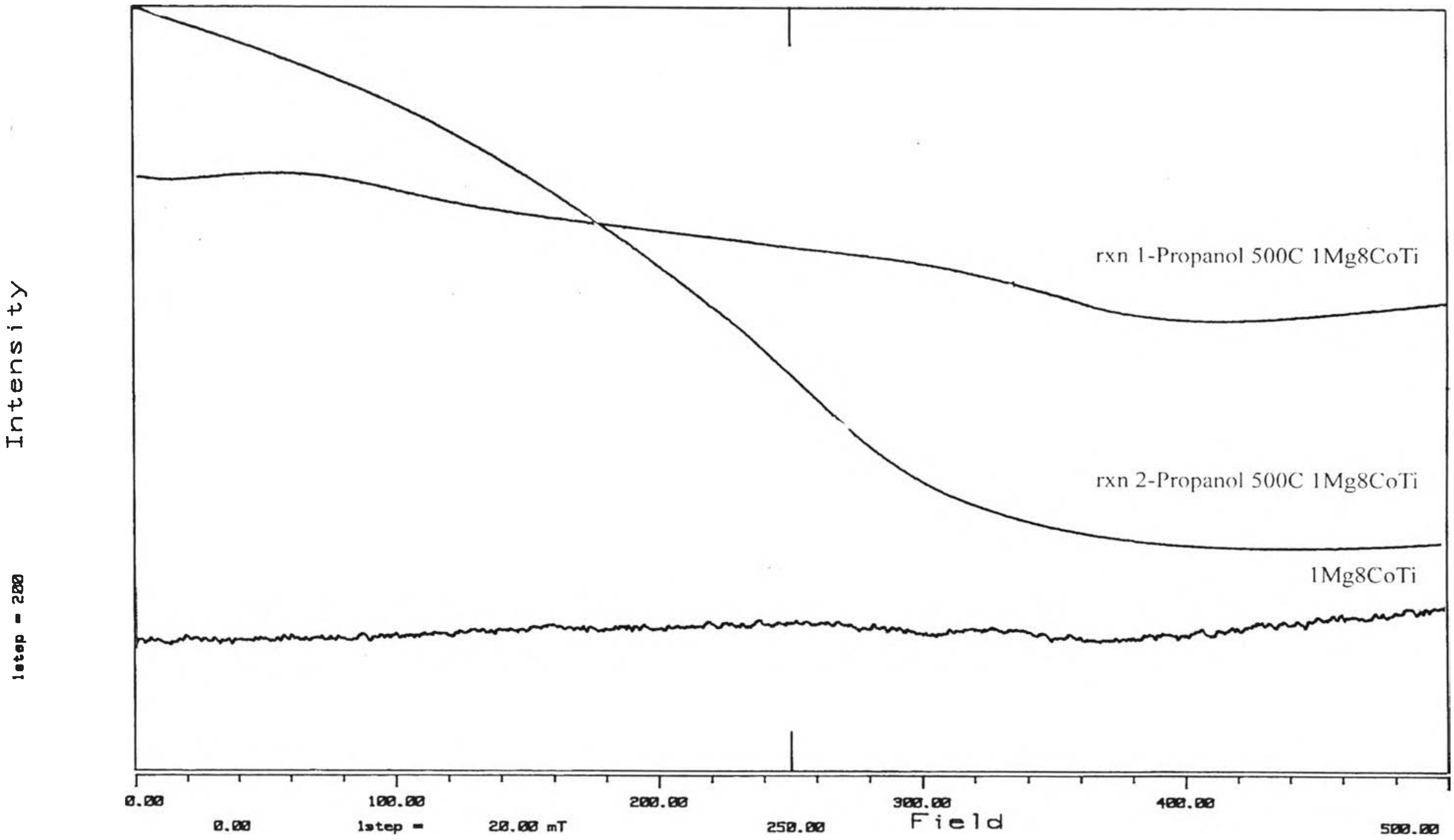

Figure 5.28 ESR spectra of used 1Mg8CoTi catalysts on 1- propanol and 2-propanol at 500 °C

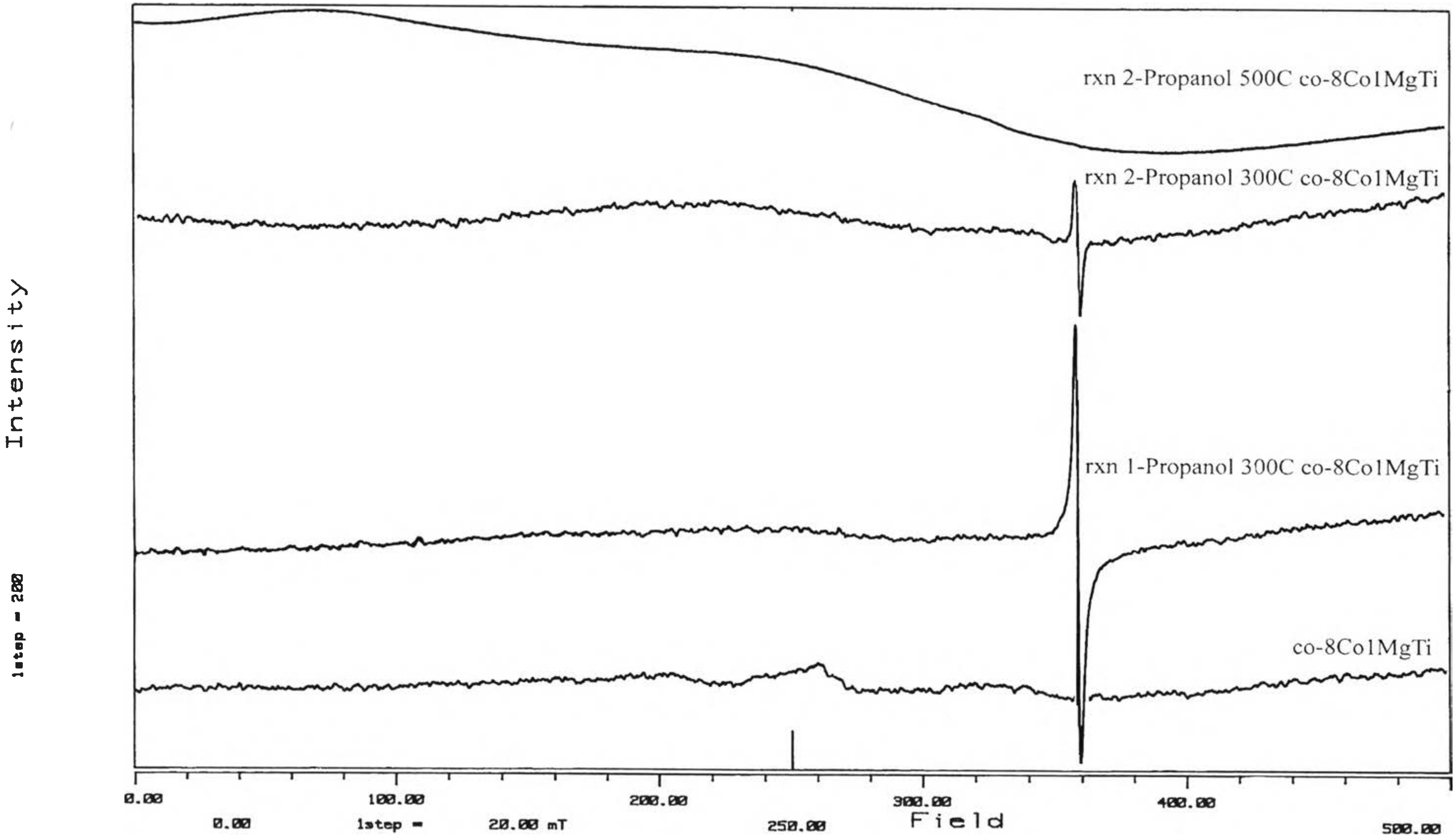

Figure 5.29 ESR spectra of used co-8Co1MgTi catalysts on 1- propanol and 2-propanol at 300 and 500 °C

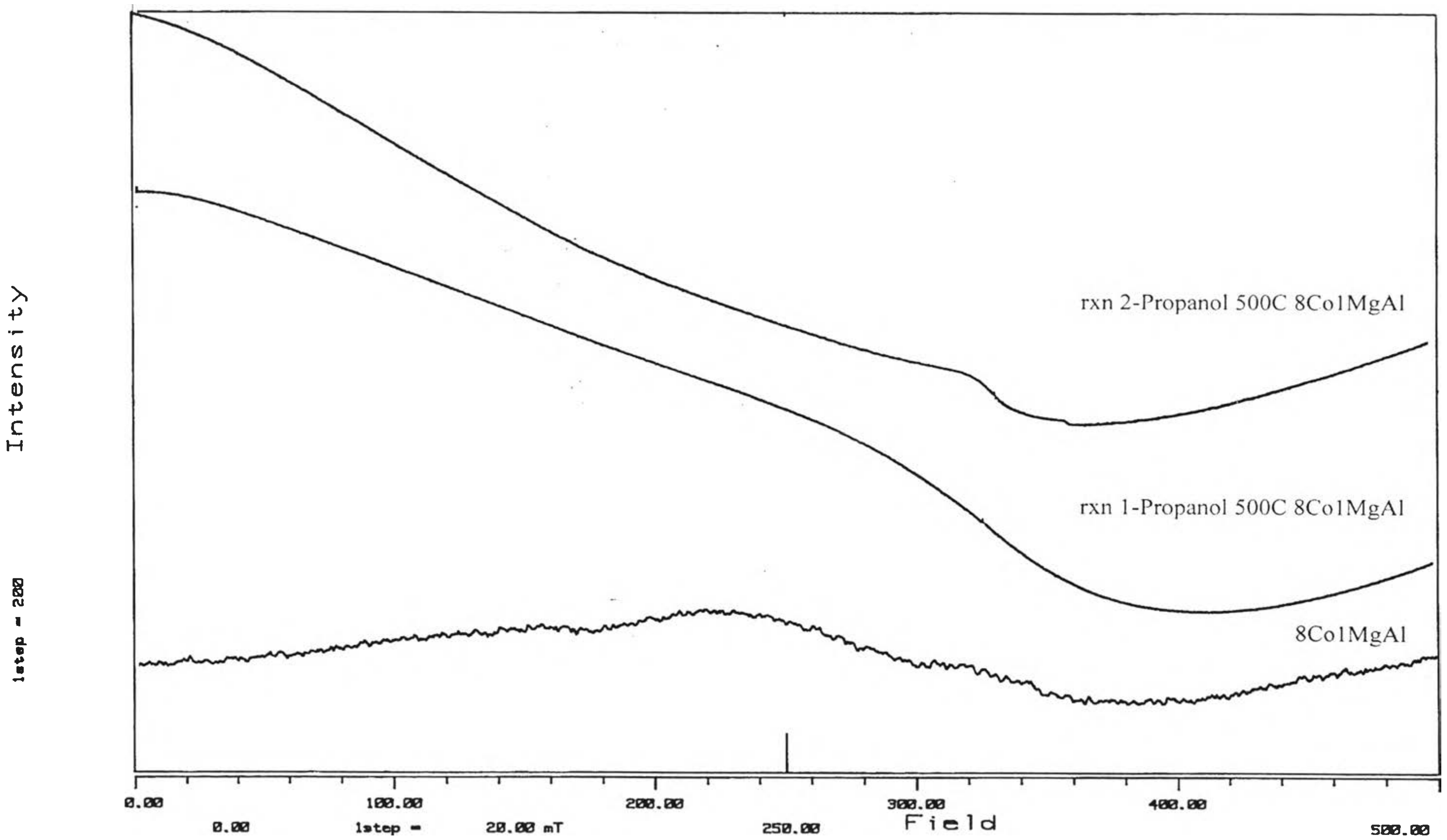

Figure 5.30 ESR spectra of used 8Co1MgAl catalysts on 1- propanol and 2-propanol at 300 and 500 °C

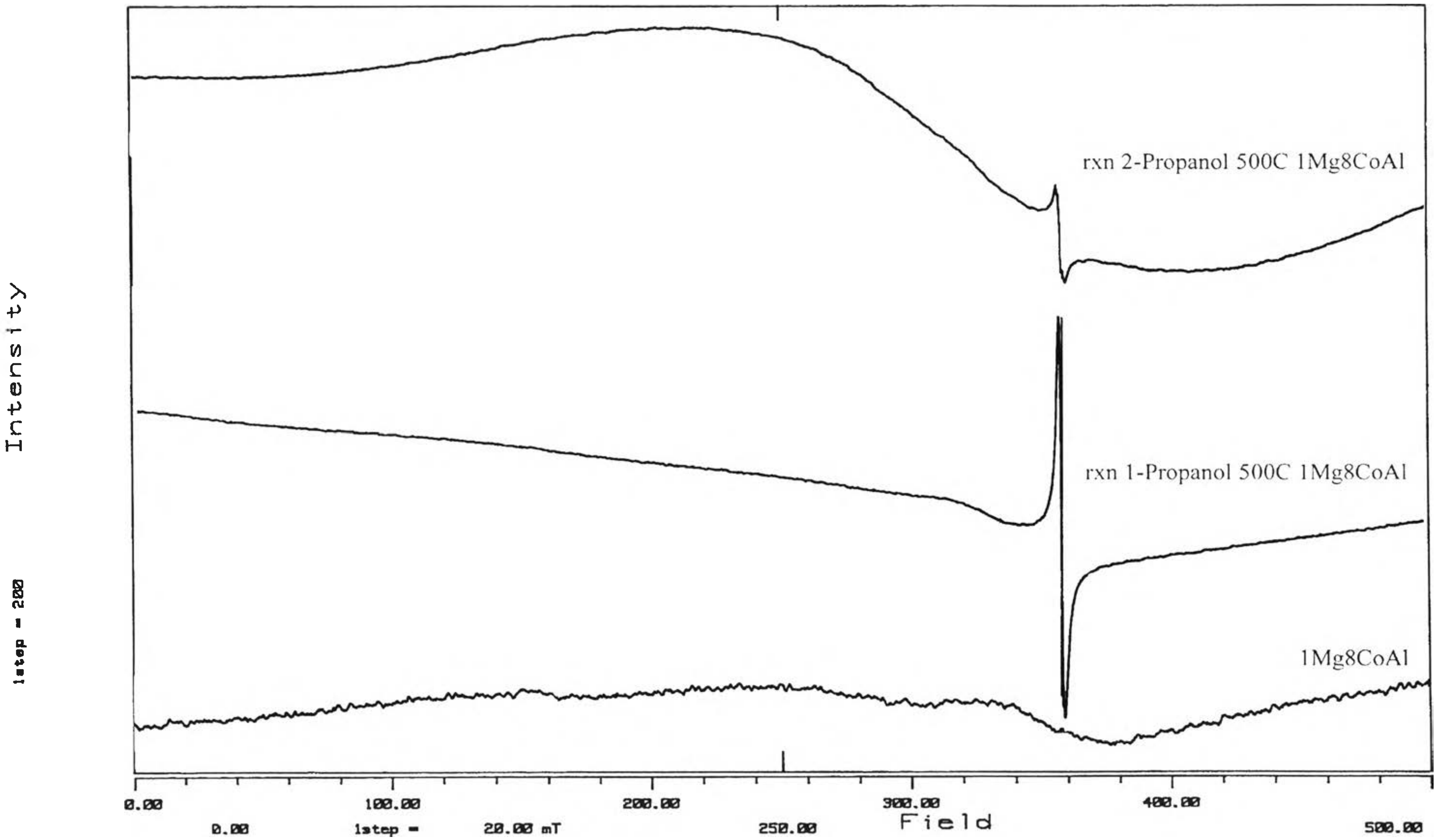

Figure 5.31 ESR spectra of used 1Mg8CoAl catalysts on 1- propanol and 2-propanol at 300 and 500 °C

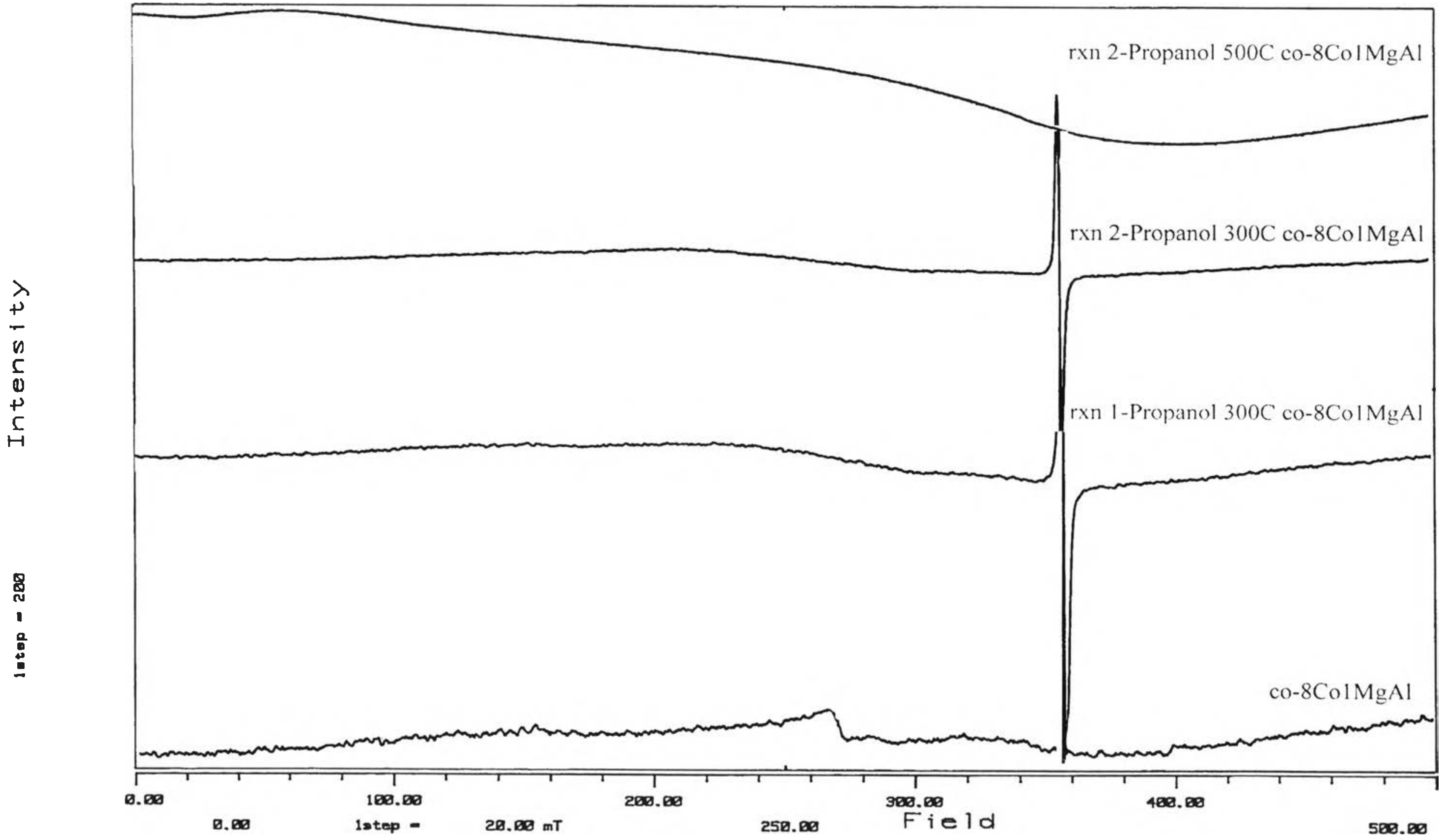

Figure 5.32 ESR spectra of used co-8Co1MgAl catalysts on 1- propanol and 2-propanol at 300 and 500 °C

5.2.5 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 wave number of 400-2000 cm^{-1}.

Figure 5.29 shows the IR spectra of JRC-TiO4, 8Co1MgTi, 1Mg8CoTi and co-8Co1MgTi. The IR absorption bands are measured at 520 and 620 cm^{-1}. The absorption peaks of 8Co1MgTi, 1Mg8CoTi, co-8Co1MgTi catalysts (figures 5.33) are detected at 580, 667cm^{-1} and also exhibits the same pattern as TiO_2. From literature reviews, 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 Co_3O_4 on the TiO_2 surface for all Co-Mg-O/ TiO_2 system.

The IR spectra of JRC-AlO2, 8Co1MgAl, 1Mg8CoAl and co-8Co1MgAl catalysts are shown in figure 5.34. The IR absorption bands of cobalt oxide are also found in Co-Mg-O/Al_2O_3 samples. It is indicated that cobalt species on these three catalysts form a Co_3O_4 crystal on Al_2O_3 support.

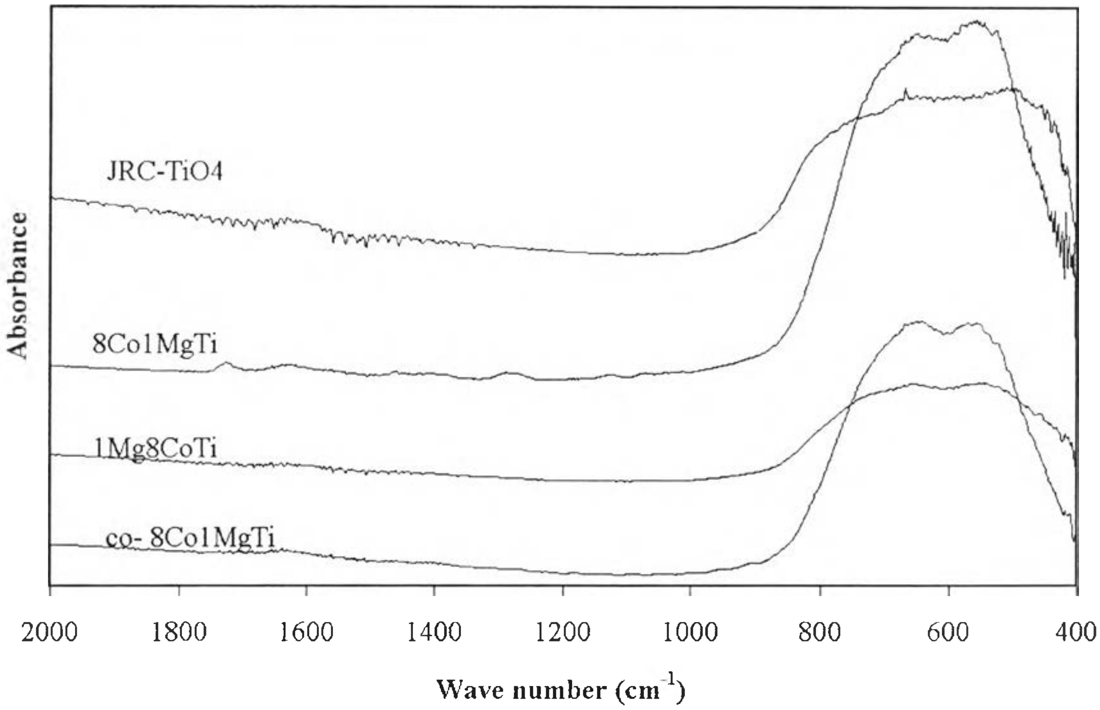

Figure 5.33 IR spectra of JRC-TiO4, 8Co1MgTi, 1Mg8CoTi and co-8Co1MgTi catalysts

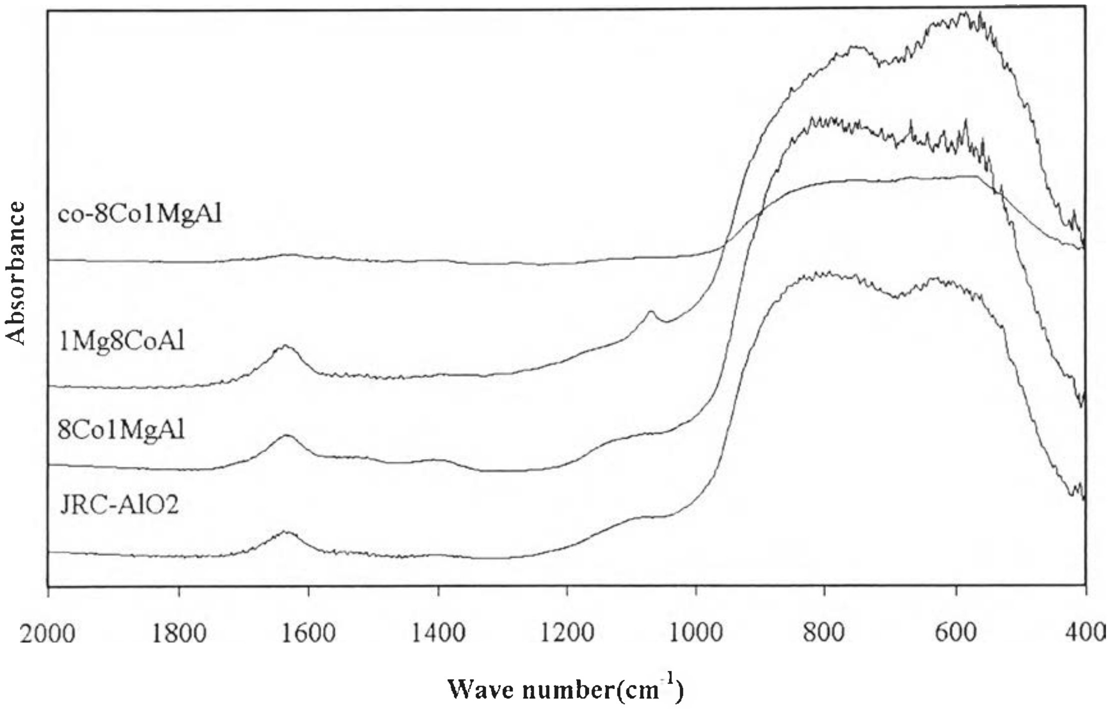

Figure 5.34 IR spectra of JRC-AlO2, 8Co1MgAl, 1Mg8CoAl and co-8Co1MgAl catalysts

5.3 Summarization of the experimental results

This research also investigates the effect of sequence of cobalt and magnesium loading on the stability of Co-Mg-O/TiO_2 and Co-Mg-O/Al_2O_3 catalysts.

From the results of 1-propanol oxidation reaction at 300°C for 48 h, there is no significant change in the 1-propanol conversion and selectivity of the main product, propionaldehyde, except in case of co-8Co1MgAl catalyst. Both 1-propanol conversion and propionaldehyde selectivity clearly shift within the first 5 h on stream reaction. Amounts of carbon deposited on catalyst surface may be the cause of catalyst deactivation.

In case of 2-propanol oxidation at 300°C for 48 h, it was found that the catalysts prepared by co-impregnation method differ from the other catalysts. For the catalysts prepared by sequential loading, the main products of 2-propanol oxidation reaction are propylene and propionaldehyde. Whereas the co-impregnation catalysts produces only propionaldehyde as main product. Independently from support effect, both TiO_2 and Al_2O_3 show consistent result of catalytic property. Another observations for this reaction are decrement in propionaldehyde selectivity and 1-propanol conversion while propylene selectivity increases over 1Mg8CoTi catalyst. Lastly, co-8Co1MgAl catalyst shows some deactivation behavior after 20 h of reaction. The conversion of 2-propanol and propionaldehyde selectivity decrease. This might be due to some carbon deposited on the catalyst surface.

For 1-propanol oxidation reaction at 500°C for 48 h, there is no important change in 8Co1MgTi and 1Mg8CoTi. However, co-8Co1MgTi catalyst exhibits some change. The conversion decreases after the first 18 h while the selectivity of propionaldehyde enhances. This change may be due to the deactivation of the catalyst structure in part that encourages the propionaldehyde selectivity. In case of alumina supported catalysts, they show some changes in catalytic property. 8Co1MgAl and 1Mg8CoAl catalysts exhibit similar behavior. The conversion of 1-propanol rapidly decreases after the first 20 h of reaction. Selectivity of acetaldehyde decreases while propionaldehyde selectivity enhances. The different between these 2 catalysts is the propionaldehyde selectivity, it is higher in case of 1Mg8CoAl. More amounts of carbon deposited on 8Co1MgAl catalyst the cause of this different. It should be noted that the surface areas of both catalysts substantially reduce, this may be another cause for the deactivation of these catalysts. For co-8Co1MgAl catalyst system, it was found that only propionaldehyde is the main product. The conversion of 1-propanol decreases within the first 9 h whereas the selectivity to propionaldehyde steadily rises in the first 4 h.

The oxidation reaction of 2-propanol at 500°C for 48 h shows different result. For 8Co1MgTi catalyst, the conversion of 2-propanol increases in the last 20 h. On the contrary, propionaldehyde selectivity decreases while propylene selectivity increases. These changes may be due to decrement of surface area and coke deposited on the catalyst. In case of 1Mg8CoTi catalyst, the conversion decreases after 17 h of reaction due to carbon deposited on the catalyst and phase transformation of the support. Co-8Co1MgTi shows a small deviation in the last 8 h of reaction. 2-propanol conversion slightly decreases whereas propionaldehyde selectivity increases. Amounts of carbon deposited on the catalyst may affect the catalytic stability of co-8Co1MgTi catalyst. Substantial change in conversion and main product selectivity of 1-propanol oxidation over 8Co1MgAl might be due to amount of carbon deposited on catalyst. 1Mg8CoAl and co-8Co1MgAl exhibit same stability trend. The conversion of 2-propanol decreases while selectivity of the main product remains constant. The causes are surface area decrement and deposited carbon on the catalyst.