CHAPTER V

RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two parts, the characterization of 8Co/MgO, 8Co/SiO$_2$, and 8Co/γ-Al$_2$O$_3$ catalysts and the catalytic oxidation reaction of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol.

5.1 Catalyst characterization

5.1.1 Determination of metal content and BET surface area of catalyst

The metal composition and surface area of 8Co/MgO, 8Co/SiO$_2$, and 8Co/γ-Al$_2$O$_3$ catalysts, which are analyzed by Atomic Absorption Spectroscopy (AAS) and BET surface area, respectively, are summarized in Table 5.1.

Table 5.1 The metal composition and BET surface area of 8Co/MgO, 8Co/SiO$_2$, and 8Co/γ-Al$_2$O$_3$ catalysts

Catalyst	%Cobalt content	BET surface area (m^2/g)	Average pore diameter (Å)
MgO	-	27	179
8Co/MgO	7.4	50	118
SiO$_2$	-	289	163
8Co/SiO$_2$	7.6	260	158
γ-Al$_2$O$_3$	-	313	64
8Co/γ-Al$_2$O$_3$	7.7	252	73

The data show that the cobalt contents in various supported cobalt oxide catalysts are close to the calculation. The surface area of 8Co/MgO catalyst increases when compare with MgO support while 8Co/SiO$_2$, and 8Co/γ-Al$_2$O$_3$ catalysts have lower surface area than SiO$_2$ and γ-Al$_2$O$_3$ supports, respectively.

5.1.2 X-ray Diffraction (XRD)

The crystal structure of catalyst was identified by X-ray diffraction technique. Figures 5.1-5.6 reveal the results of XRD spectra of catalysts (MgO, 8Co/MgO, SiO_2, 8Co/SiO_2, γ-Al_2O_3, and 8Co/γ-Al_2O_3 catalysts).

The XRD pattern of MgO catalyst is presented in figure 5.1. The XRD pattern of MgO shows 5 peaks at $36.5°$, $43°$, $62°$, $75°$, and $78°$. As presented in the same figure, the XRD pattern of 8Co/MgO catalyst is the same as MgO support but the level of intensity is lower than MgO support.

From the XRD results in figure 5.2 we can conclude that the crystalline of cobalt oxide is unobservable. Thus it can be suggested that the crystalline of cobalt oxide is too small or the 8Co/MgO catalyst forms a thin layer of some Co-Mg-O compounds on the surface of catalyst so that XRD diffraction can not measure. The structure of 8Co/MgO catalyst is similar to MgO, but more amorphous.

In the case of 8Co/SiO_2 catalyst, the XRD pattern shown in figure 5.4 is amorphous as SiO_2 support, figure 5.3. The characteristic peak of cobalt oxide is not observed and this can be explained as in the case of 8Co/MgO catalyst.

Figures 5.5-5.6 show XRD patterns of γ-Al_2O_3 and 8Co/γ-Al_2O_3 catalysts. Characteristic lines of γ-Al_2O_3 are observed in both 8Co/γ-Al_2O_3 and γ-Al_2O_3 catalysts. The XRD pattern of 8Co/γ-Al_2O_3 catalyst does not show any lines due to crystalline cobalt oxide phase or any compounds of the same with the support. The absence of characteristic peaks of cobalt oxide indicates that the cobalt oxide is either in microcrystalline state or 8Co/γ-Al_2O_3 catalyst forms a thin layer of some compounds between cobalt and γ-Al_2O_3 distribute on the surface of catalyst so that XRD diffraction can not detect.
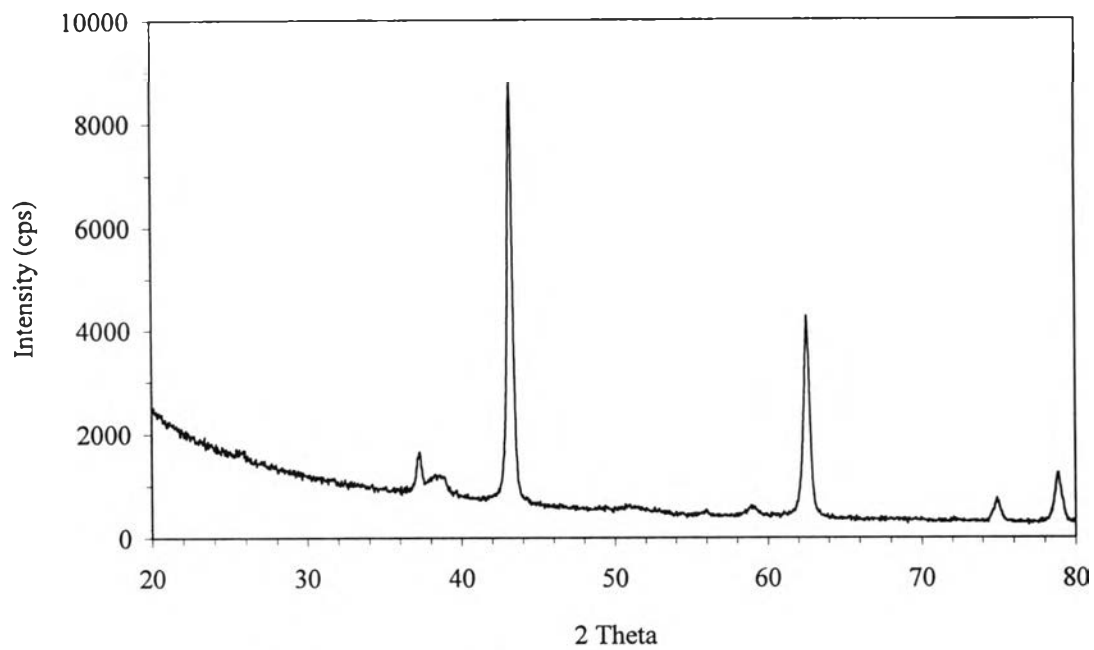
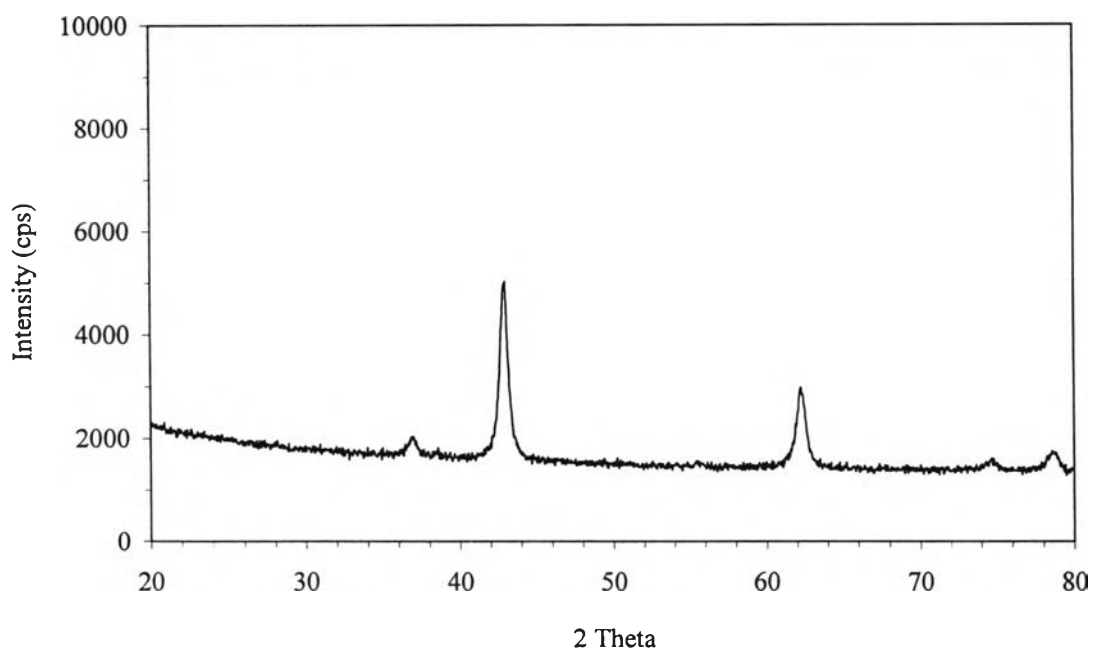**Figure 5.1** The XRD pattern of MgO catalyst.

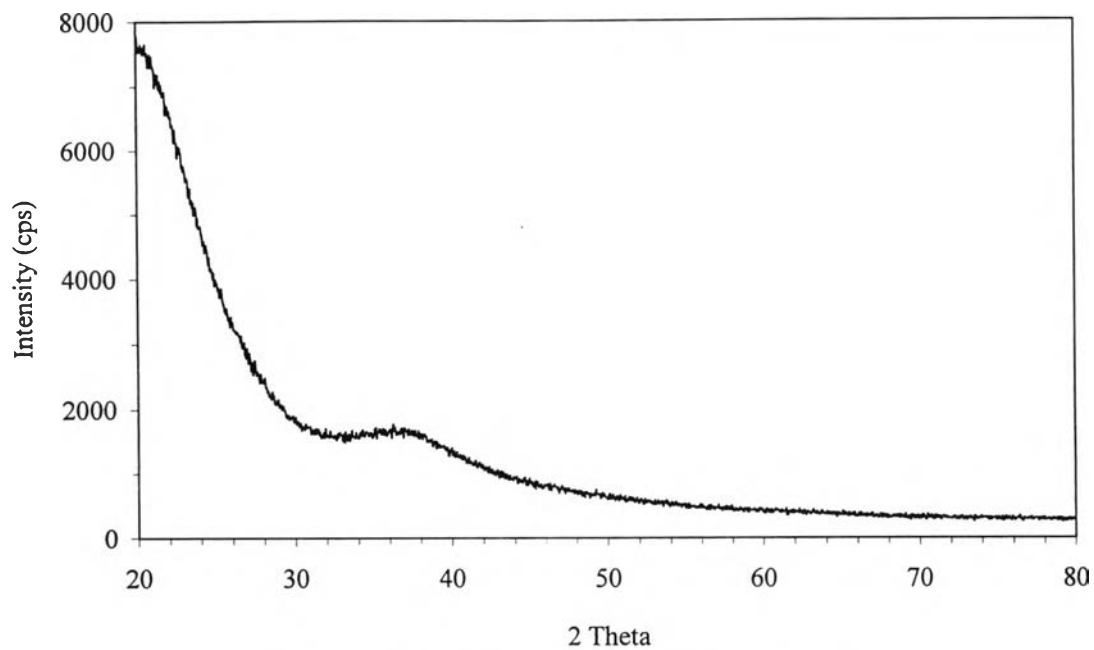**Figure 5.2** The XRD pattern of 8Co/MgO catalyst.
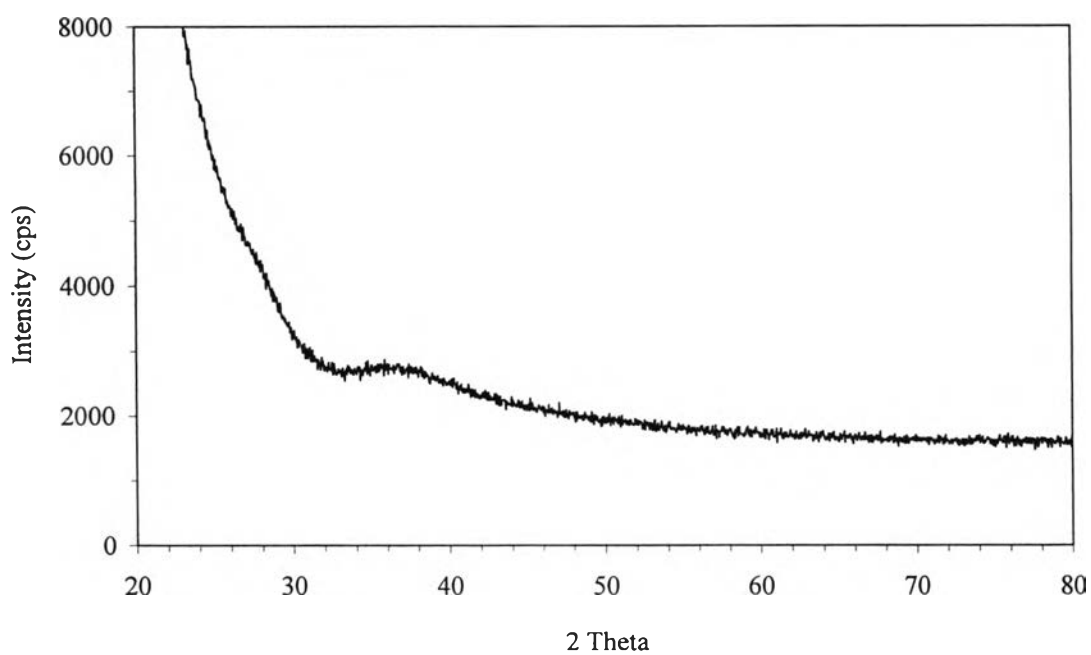
Figure 5.3 The XRD pattern of SiO_2 catalyst.

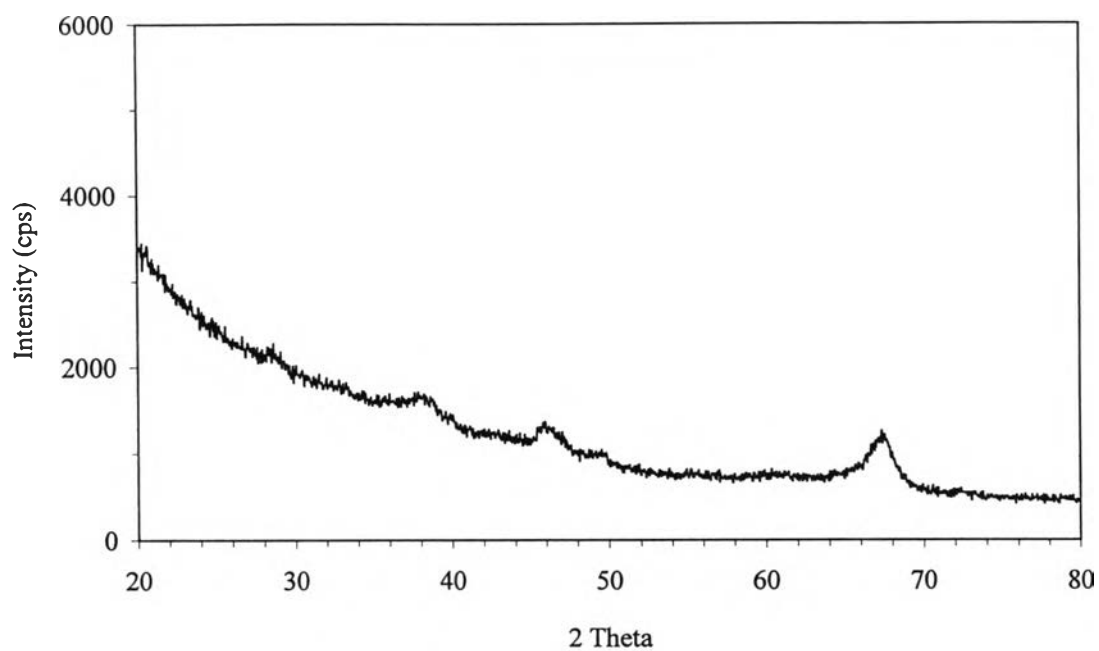**Figure 5.4** The XRD pattern of $8Co/SiO_2$ catalyst.

Figure 5.5 The XRD pattern of γ-Al_2O_3 catalyst.
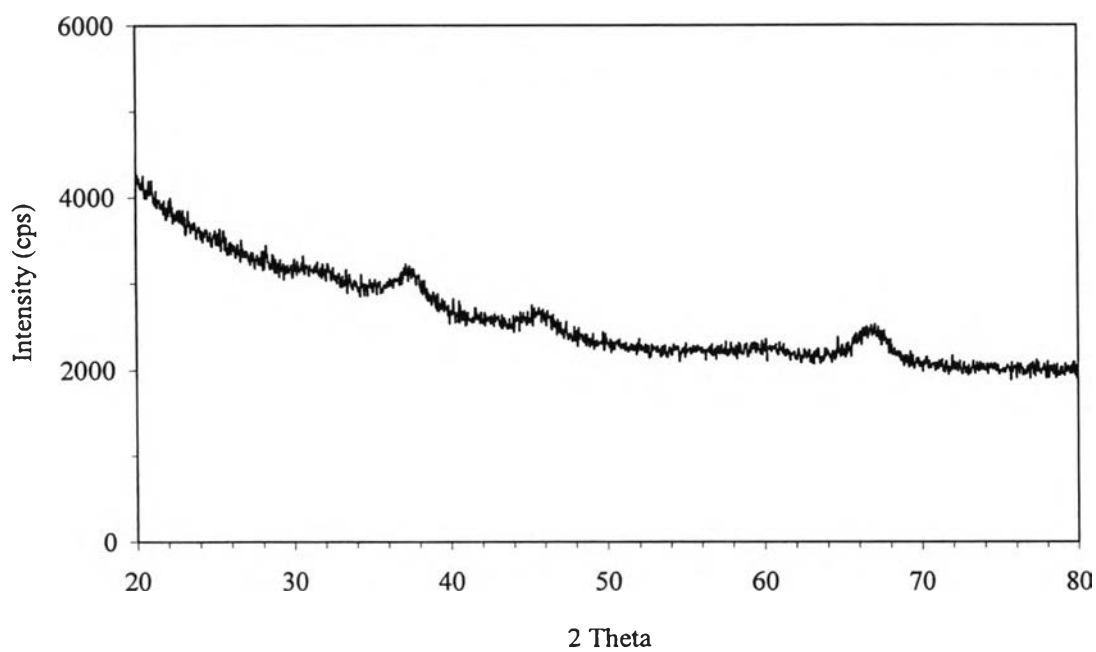

Figure 5.6 The XRD pattern of $8Co/\gamma$-Al_2O_3 catalyst.

5.1.3 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 wavenumber of 400-2000 cm^{-1}.

Figure 5.7 shows the IR spectrum of MgO support. The IR absorption bands are measured in the region 400-800, 1130, and 1480 cm^{-1}. The absorption peaks of 8Co/MgO catalyst (figure 5.8) are detected in the region 400-800, 880, 1130, and 1480 cm^{-1} also exhibits the same pattern as MgO. From literature research, the IR absorption bands of cobalt oxide occurs at 385, 580, and 667 cm^{-1} [Busca et al. (1990)]. This means that the absorption frequency of cobalt oxide in 8Co/MgO catalyst is not measurable because in these regions since the IR spectra of cobalt oxide may be hidden by the absorption of MgO.

The IR spectra of SiO_2, 8Co/SiO_2, γ-Al_2O_3, and 8Co/γ-Al_2O_3 catalysts are shown in figures 5.9-5.12. The IR absorption bands of cobalt oxide are not found in 8Co/SiO_2 and 8Co/γ-Al_2O_3 samples. It is suggested that the IR spectrum of cobalt oxide occurs at the same bands of those of SiO_2 and γ-Al_2O_3 supports.
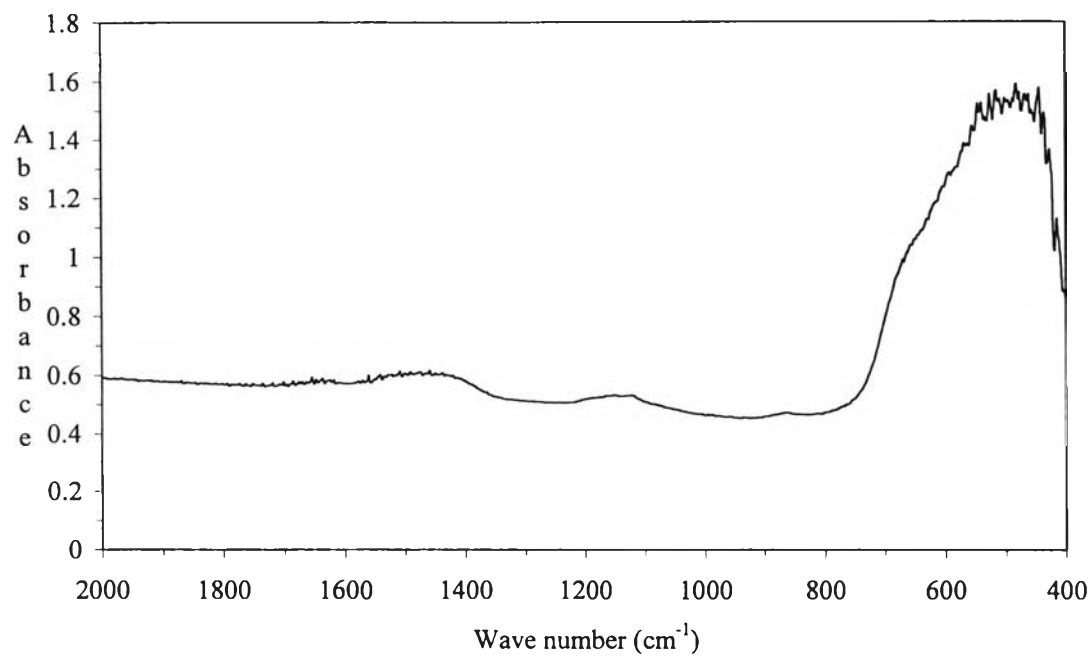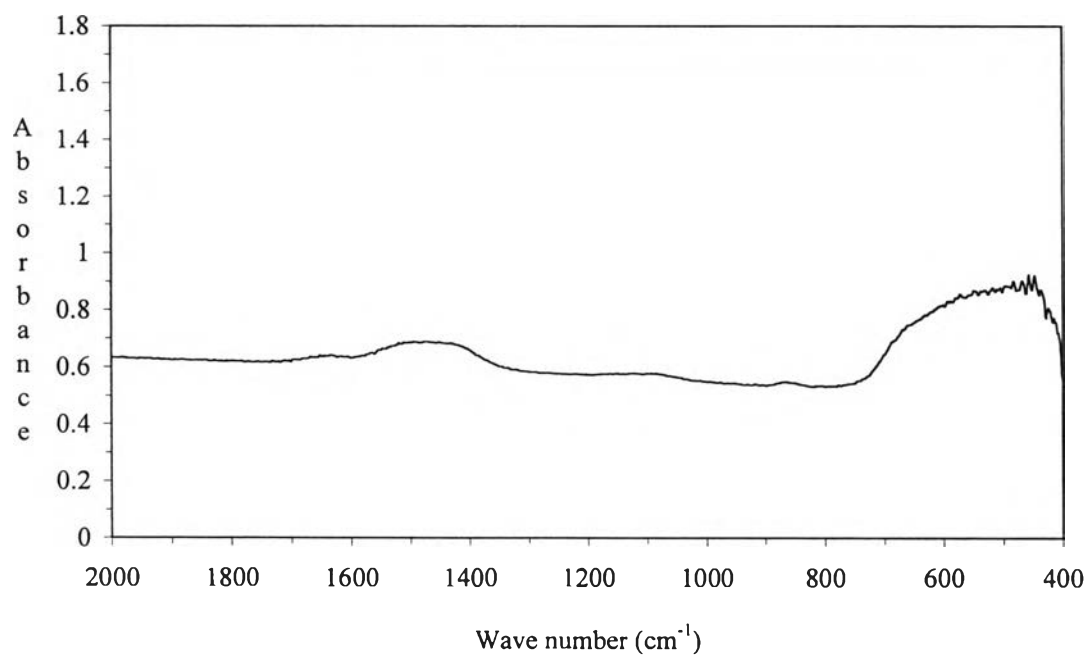
Figure 5.7 IR spectrum of MgO catalyst.

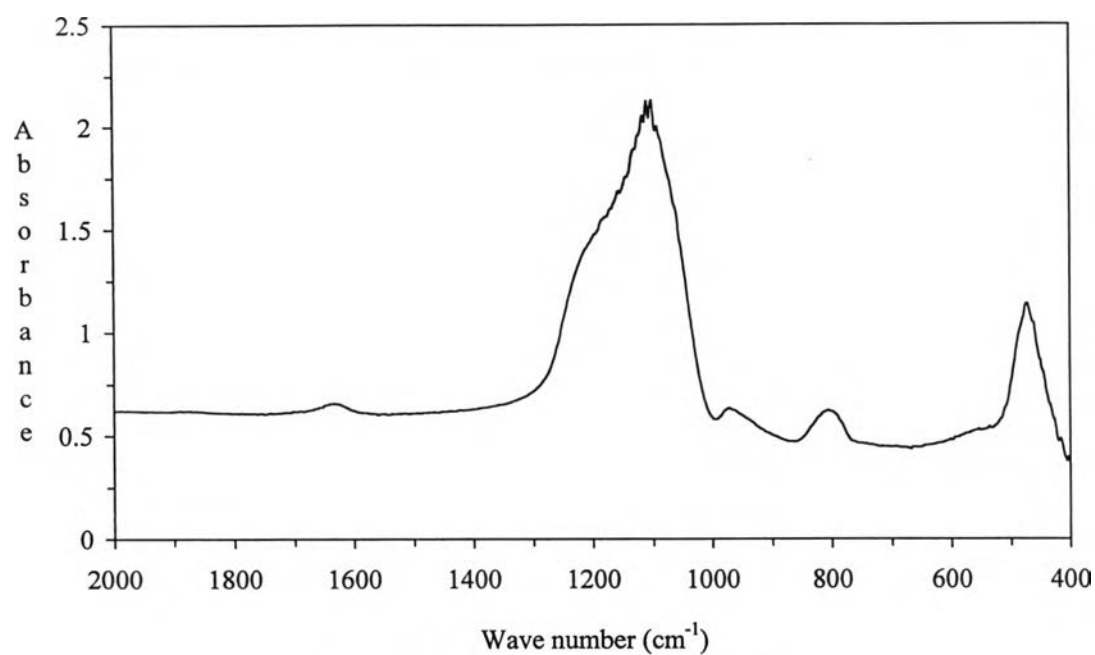**Figure 5.8** IR spectrum of 8Co/MgO catalyst.

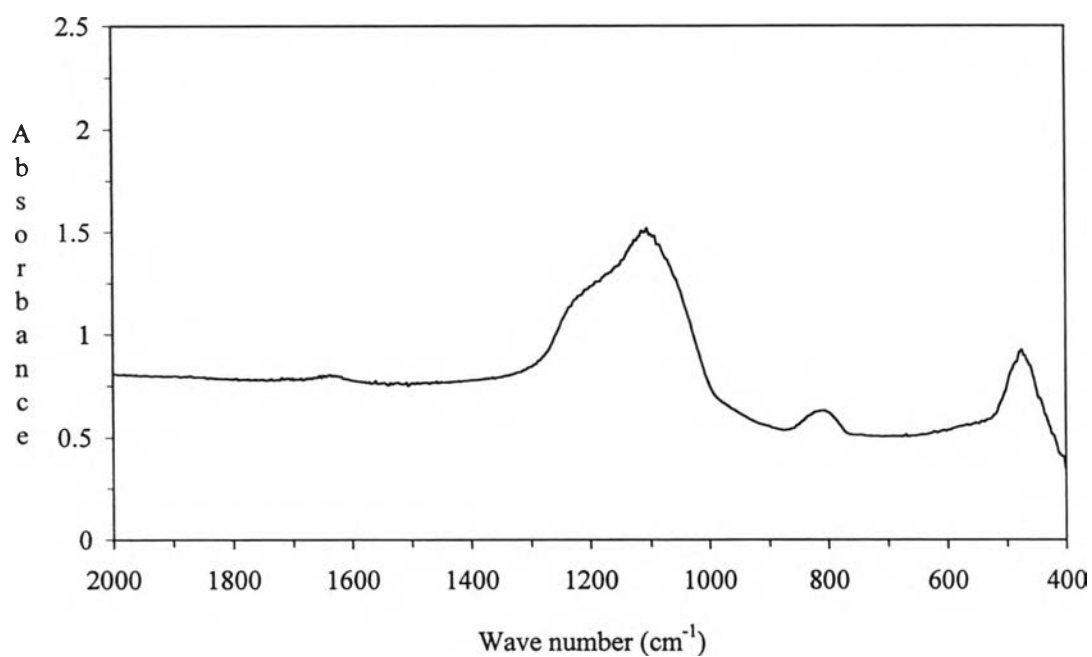**Figure 5.9** IR spectrum of SiO_2 catalyst.

Figure 5.10 IR spectrum of $8Co/SiO_2$ catalyst.
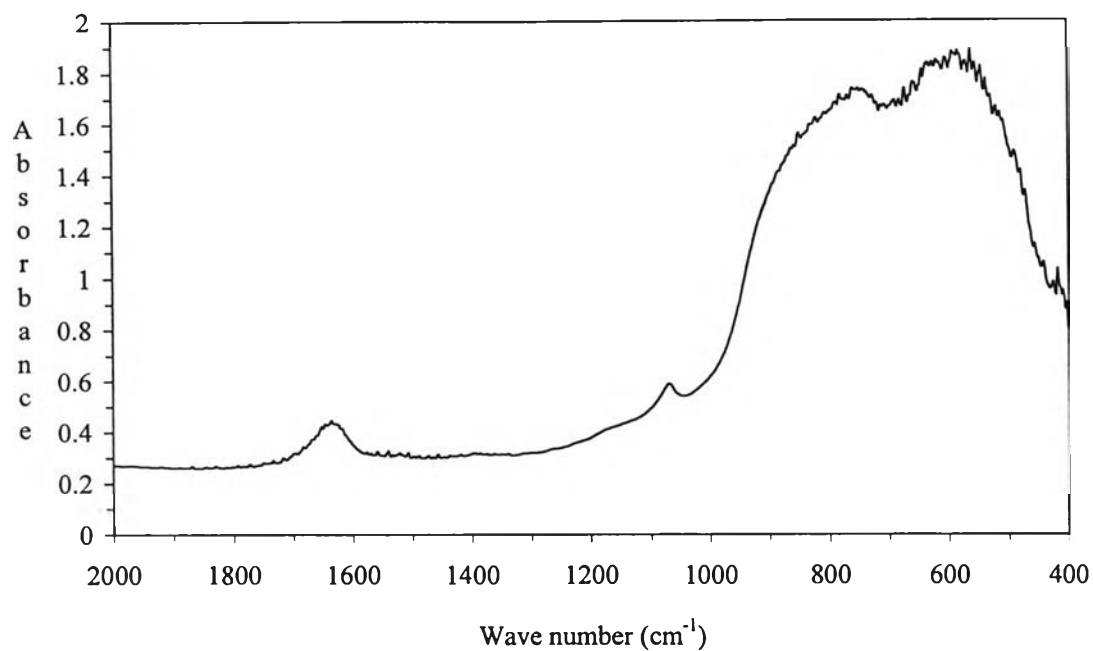
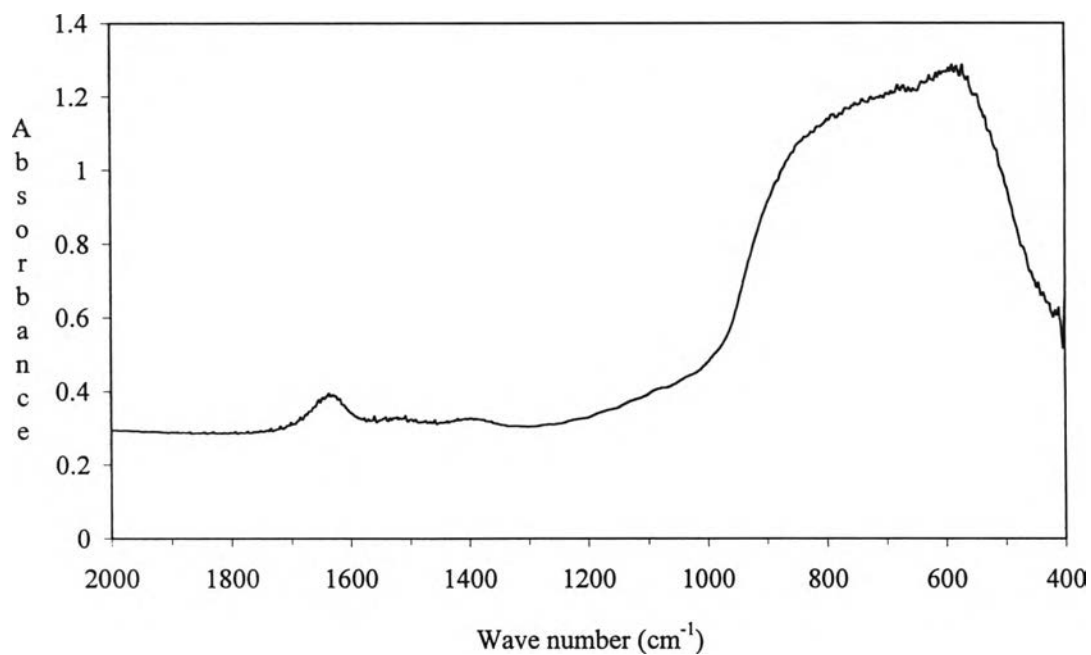**Figure 5.11** IR spectrum of Al₂O₃ catalyst.

Figure 5.12 IR spectrum of 8Co/Al₂O₃ catalyst.

5.2 Oxidation reaction

In this part, the oxidation properties of 8Co/MgO, 8Co/SiO₂, and 8Co/γ-Al₂O₃ catalysts are studied by using the oxidation reaction of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol as test reaction. The calculation in appendix B shows that there is no effect of internal and external diffusion under the reaction condition.

5.2.1 Methanol oxidation

- **8Co/MgO catalyst**

Figure 5.13 shows the activity of 8Co/MgO catalyst for methanol oxidation reaction. The conversion of methanol increases from 2% to 22% at the temperature range 200-300°C and rapidly increases to 94% at 400°C. Above 400°C, methanol conversion approaches 100% at 500°C. At the initial reaction temperature (200-300°C) the main product is CO_2 and there are some formation of methane. When increasing reaction temperature, the selectivity to CO_2 gradually declines to 79% while methane selectivity enhances to 18% at 500°C.

- **8Co/SiO₂ catalyst**

The catalytic property of 8Co/SiO₂ catalyst on methanol oxidation is illustrated in figure 5.14. In the reaction temperature range 200-300°C methanol conversion rises from 5% to 29% and significantly increases to 72% at 400°C. Beyond 400°C, the conversion of methanol slightly increases up to 100% at 500°C. CO_2 selectivity gradually goes down from 98% to 84% in the temperature range 200-500°C. On the other hand, the selectivity to methane slightly rises from 2% to 14% at all reaction temperature range.
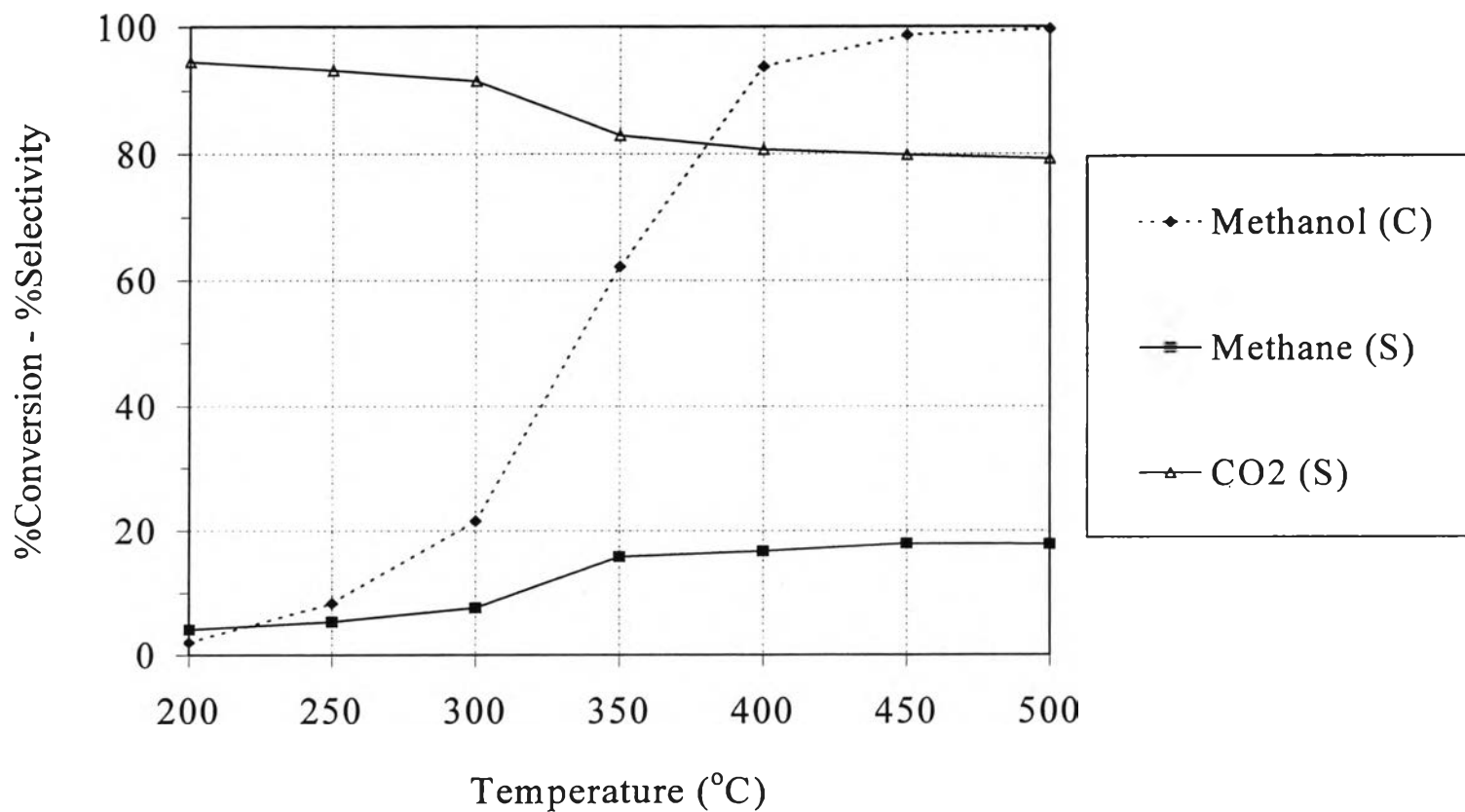
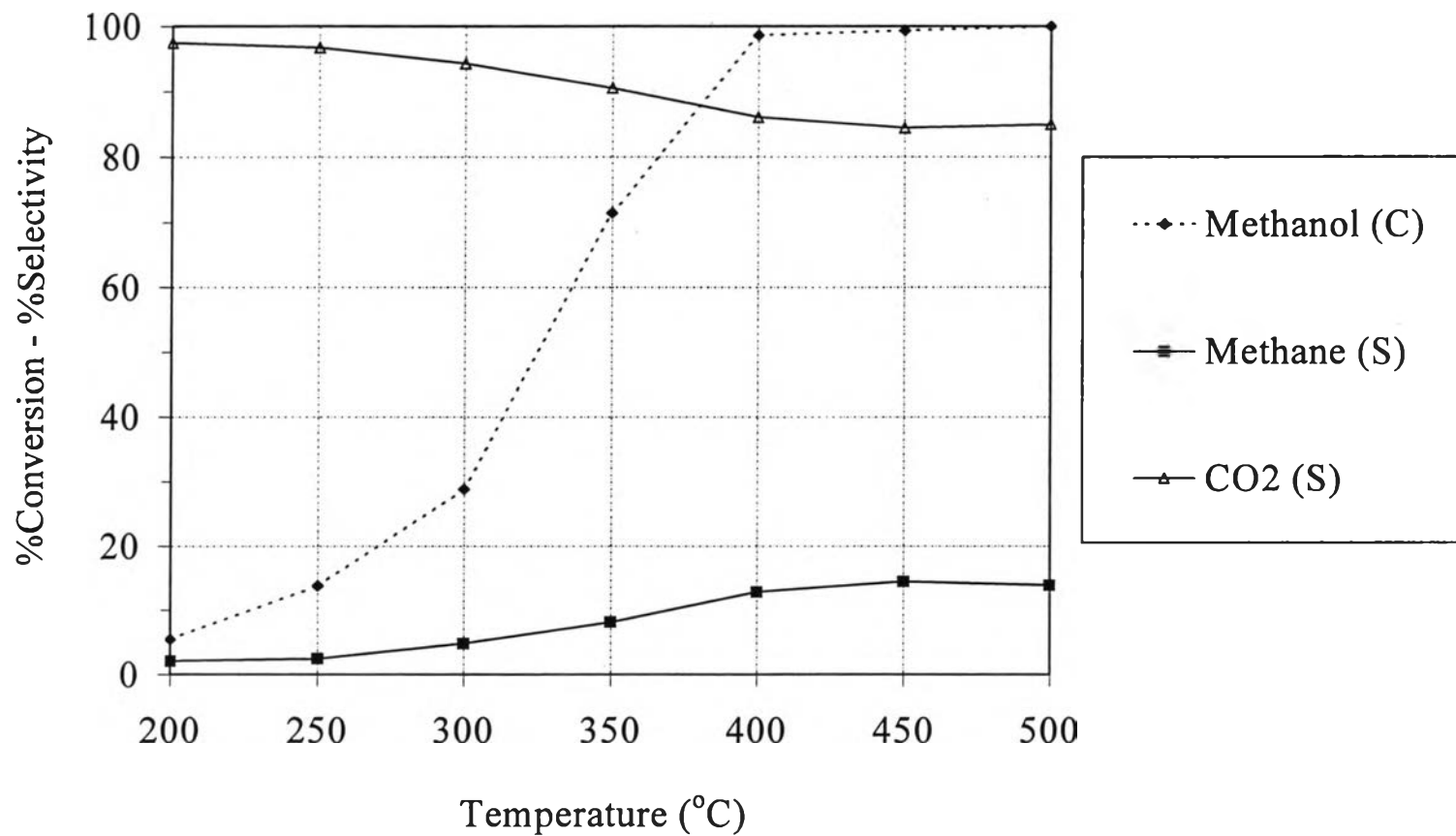**Figure 5.13** Conversion (C) of methanol and product selectivities (S) on 8Co/MgO catalyst in the methanol oxidation.

Figure 5.14 Conversion (C) of methanol and product selectivities (S) on 8Co/SiO$_2$ catalyst in the methanol oxidation.

- **8Co/γ-Al$_2$O$_3$ catalyst**

The behavior of 8Co/γ-Al$_2$O$_3$ catalyst for methanol oxidation is described in figure 5.15. The methanol conversion increases from 9% to 18% and rapidly rises to 91%, and then slightly enhances up to 100% at the temperature range 200-250, 250-350, 350-500°C, respectively. CO$_2$ is the only major product over all reaction temperature range. However, the selectivity to CO$_2$ gradually decreases when increasing the reaction temperature while methane selectivity slightly rises until to 6% at 500°C.

From the above results, it is shown that the activity patterns of these catalysts for methanol oxidation are almost the same. Mostly, methanol is converted to CO$_2$ and small amount of methane over the whole reaction temperature.

5.2.2 Ethanol oxidation

- **8Co/MgO catalyst**

Figure 5.16 shows the catalytic activity of 8Co/MgO catalyst for ethanol oxidation reaction. At low reaction temperature the conversion of ethanol steadily increases from 4% to 20% with increasing reaction temperature from 200°C to 300°C. In the temperature range 300-400°C the ethanol conversion rapidly increases from 20% to 75%. Beyond 400°C, the conversion of ethanol gradually rises up to 83% at 500°C.

At low ethanol conversion (200-300°C) the major reaction product is acetaldehyde and there is some formation of other reaction products i.e., methane, ethylene, and CO$_2$ while at high ethanol conversion (400-500°C) the main product is still acetaldehyde and with traces of methane and ethylene. Consequently, the selectivity of acetaldehyde moderately falls from 98% to 68% and the selectivities of CO$_2$, ethylene, and methane slightly rise from 1% to 18%, 0% to 7%, and 0% to 5%,
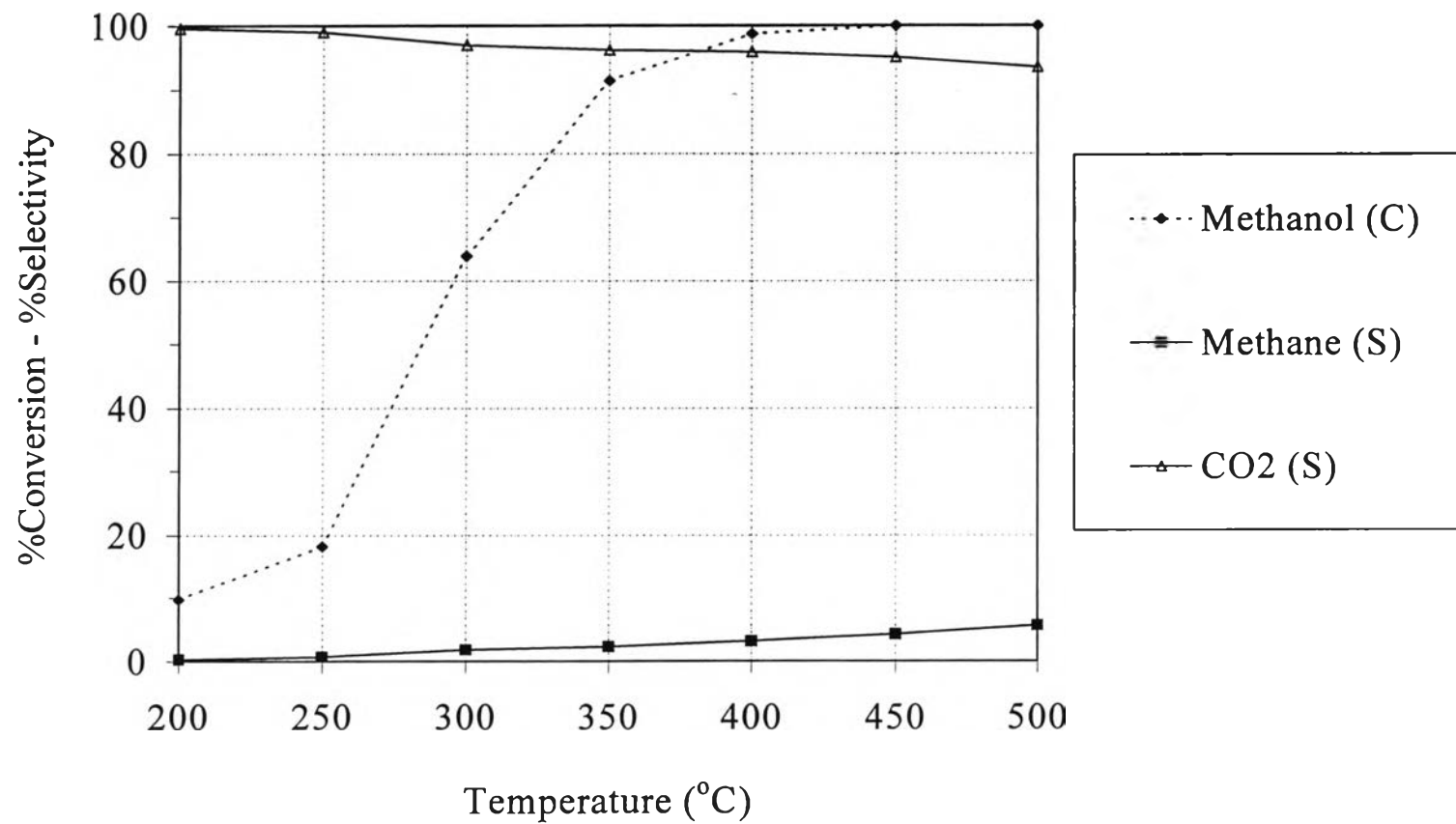
Figure 5.15 Conversion (C) of methanol and product selectivities (S) on $8Co/\gamma\text{-}Al_2O_3$ catalyst in the methanol oxidation.

respectively with increasing reaction temperature from 200-500°C. From these results the maximum yield of acetaldehyde is ca. 58% at 400°C.

- **8Co/SiO$_2$ catalyst**

The result of the catalytic oxidation of ethanol on 8Co/SiO$_2$ catalyst is shown in figure 5.17. At low reaction temperature the activity of 8Co/SiO$_2$ catalyst steadily increases from 7% to 22% ethanol conversion on the increase of reaction temperature from 200°C to 300°C. The conversion of ethanol significantly rises from 22% to 84% in the temperature range 300-400°C and then gradually increases up to 95% at 500°C.

At low ethanol conversion (200-300°C) the major product is acetaldehyde and traces of CO$_2$ and ethylene whereas at high ethanol conversion (above 300°C) acetaldehyde, CO$_2$, and ethylene are the main reaction products. The selectivity to ethylene is higher than in case of 8Co/MgO catalyst over all the temperature range. Trace of methane is detected at all reaction temperature range. The maximum selectivities to CO$_2$ and ethylene are about 40% and 19% at 500°C and the maximum yield of acetaldehyde is ca. 43% at 400°C.

- **8Co/γ-Al$_2$O$_3$ catalyst**

The behavior of 8Co/γ-Al$_2$O$_3$ catalyst for ethanol oxidation is exhibited in figure 5.18. In the initial reaction temperature, the conversion of ethanol gradually increases from 10% to 12% on the increase of reaction temperature from 200°C to 250°C. When the reaction temperature is higher than 250°C the ethanol conversion of this catalyst rapidly rises to 74% at 350°C and then slightly increases up to 94% at 500°C.

At low ethanol conversion the main oxidation product is acetaldehyde with small amounts of CO$_2$ and ethylene. At high ethanol conversion (above 250°C) acetaldehyde selectivity rapidly decreases while CO$_2$ and ethylene selectivities quickly increase. The selectivity to ethylene is higher than in case of 8Co/SiO$_2$ and

8Co/MgO catalysts over all the reaction temperature range. The maximum selectivities to CO_2 and ethylene are about 28% and 41% at 500°C and the maximum yield of acetaldehyde is ca. 40% at 350°C.

From the ethanol oxidation reaction, it turns out that of 8Co/MgO catalyst provides the highest acetaldehyde formation under the oxidation condition. The maximum acetaldehyde yield is about 58% at 400°C.

5.2.3 1-Propanol oxidation

- **8Co/MgO catalyst**

Figure 5.19 shows the catalytic activity of 8Co/MgO catalyst for 1-propanol oxidation reaction. At low reaction temperature the conversion of 1-propanol steadily increases from 2% to 6% with increasing reaction temperature from 200°C to 250°C. In the reaction temperature range 250-400°C the 1-propanol conversion rapidly increases from 6% to 74%. Beyond 400°C, the conversion of 1-propanol gradually rises up to 76% at 500°C.

At low 1-propanol conversion (200-250°C) the major reaction product is propionaldehyde. Also, there are some formation of other reaction products i.e., methane, ethylene, propylene, formaldehyde, and CO_2. While at high 1-propanol conversion (400-500°C) the main products are propionaldehyde and CO_2 and with traces of methane, ethylene, propane, propylene, and formaldehyde. Consequently, the selectivity of propionaldehyde moderately falls from 91% to 68% and the selectivities of CO_2 and formaldehyde slightly rise from 5% to 20% and 0% to 4%, respectively, with increasing reaction temperature from 200-500°C. Ethylene and propylene selectivities are rather constant about 1-2% at all reaction temperature. From these results the maximum yield of propionaldehyde is ca. 53% at 400°C.
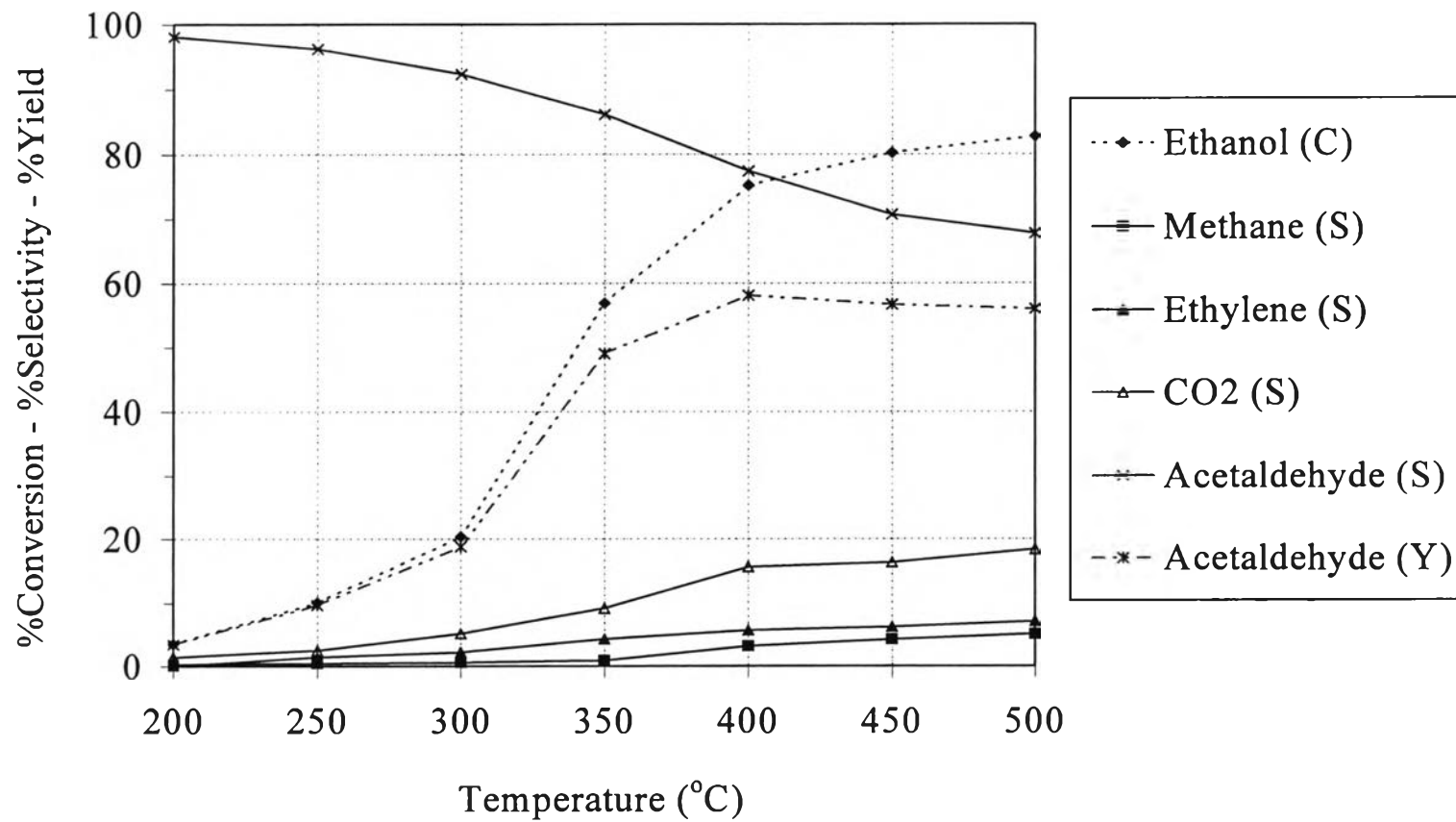
Figure 5.16 Conversion (C) of ethanol, product selectivities (S), and yield of acetaldehyde (Y) on 8Co/MgO catalyst in the ethanol oxidation.
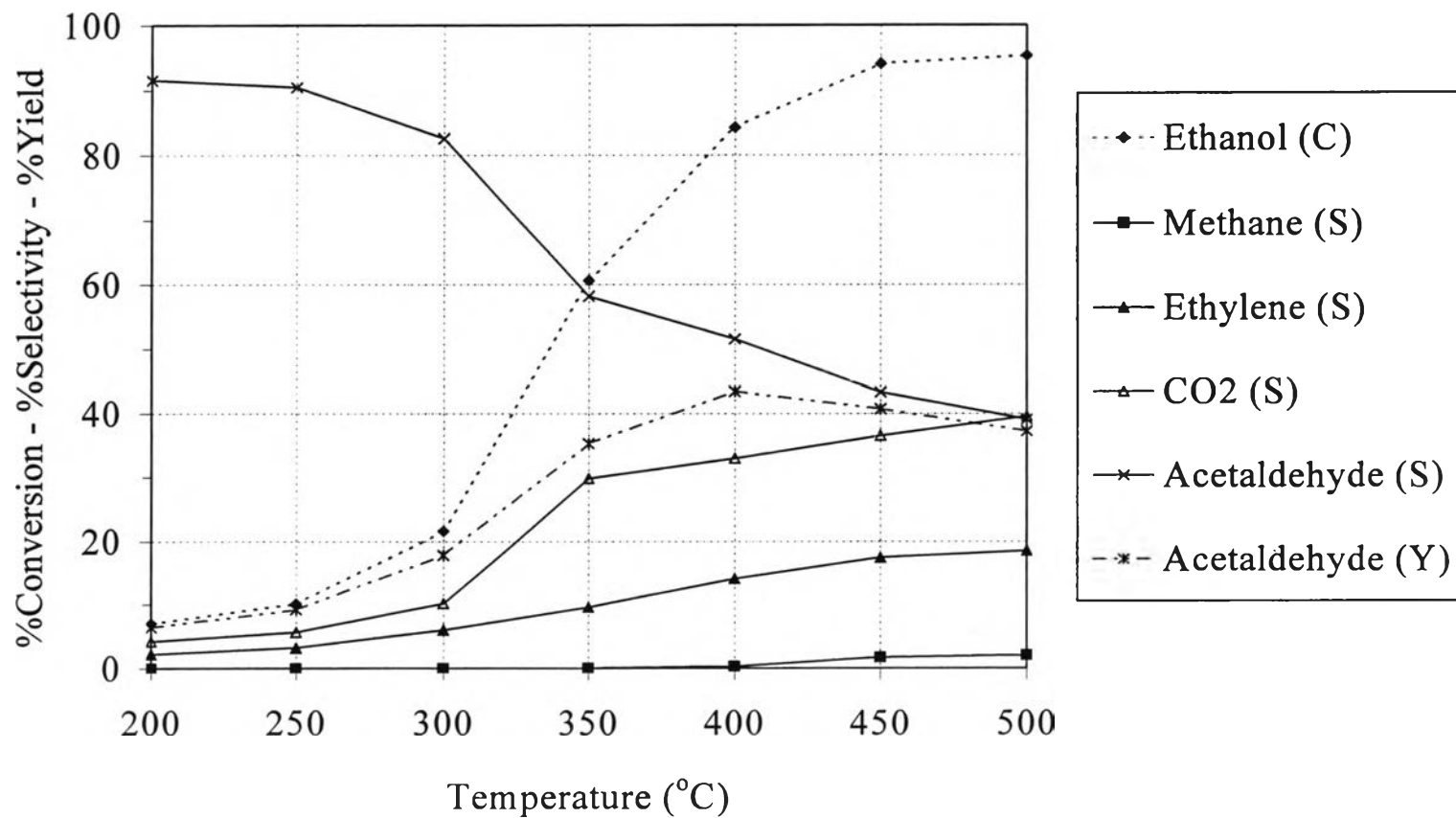
Figure 5.17 Conversion (C) of ethanol, product selectivities (S), and yield (Y) of acetaldehyde on $8Co/SiO_2$ catalyst in the ethanol oxidation.
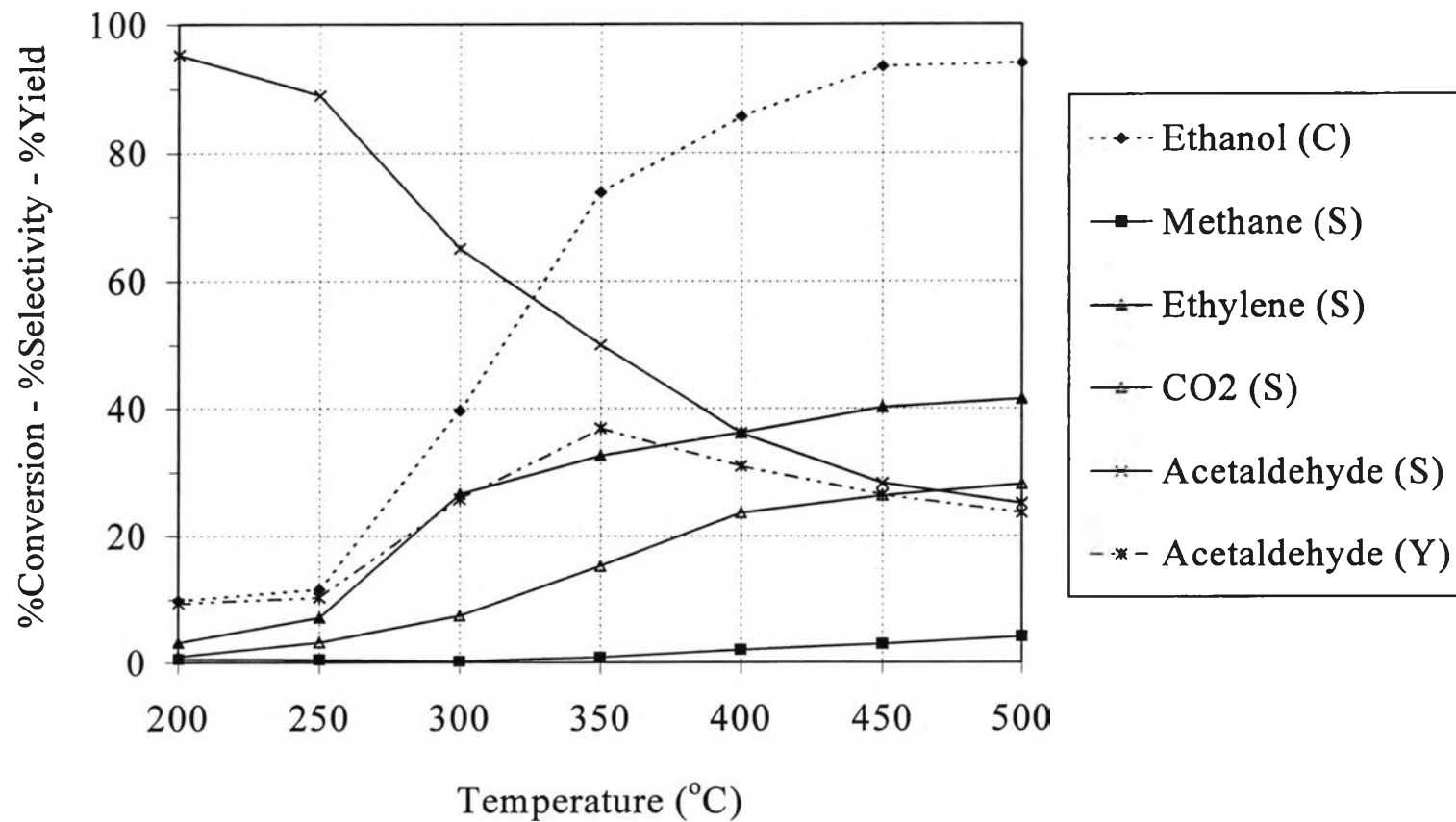
Figure 5.18 Conversion (C) of ethanol, product selectivities (S), and yield (Y) of acetaldehyde on $8Co/\gamma-Al_2O_3$ catalyst in the ethanol oxidation.
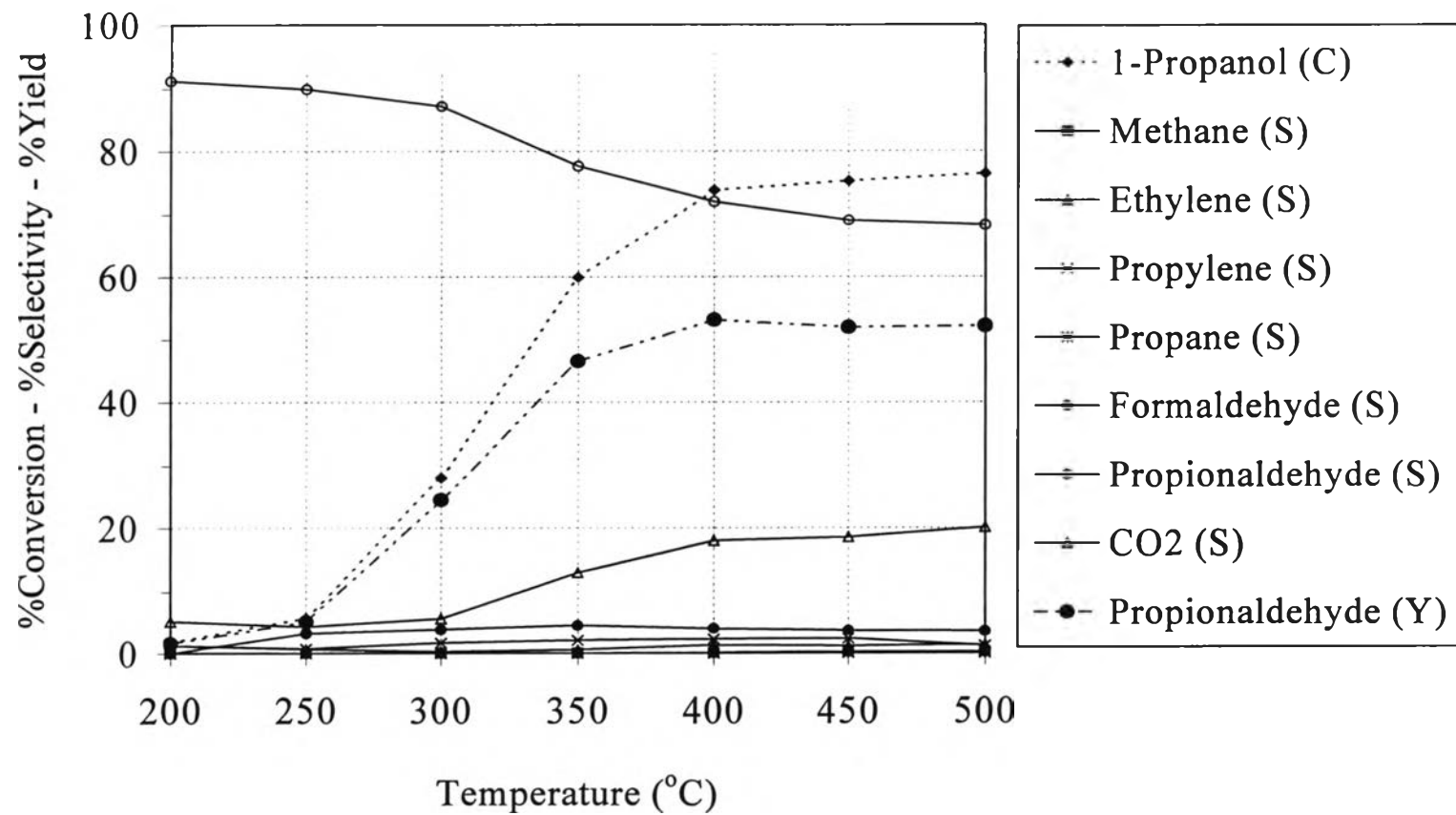
Figure 5.19 Conversion (C) of 1-propanol, product selectivities (S), and yield (Y) of propionaldehyde on 8Co/MgO catalyst in the 1-propanol oxidation.

- 8Co/SiO₂ catalyst

The result of the catalytic oxidation of 1-propanol on 8Co/SiO$_2$ catalyst is shown in figure 5.20. At low reaction temperature the activity of 8Co/SiO$_2$ catalyst steadily increases from 6% to 30% 1-propanol conversion on the increase of reaction temperature from 200°C to 300°C. The conversion of 1-propanol significantly rises from 30% to 70% in the temperature range 300-400°C and then gradually increases up to 77% at 500°C.

At low 1-propanol conversion (200-300°C) the major product is propionaldehyde and traces of CO$_2$ and propylene whereas at high 1-propanol conversion (above 300°C) propionaldehyde, CO$_2$, and propylene are the main reaction products. Traces of methane, ethylene, and formaldehyde are detected at all reaction temperature range. The selectivity to propylene is higher than in case of 8Co/MgO catalyst at all the reaction temperature range. The maximum selectivities to CO$_2$ and propylene are about 26% and 26% at 500°C and the maximum yield of propionaldehyde is ca. 37% at 400°C.

- 8Co/γ-Al₂O₃ catalyst

The behavior of 8Co/γ-Al$_2$O$_3$ catalyst for 1-propanol oxidation is exhibited in figure 5.21. In the initial reaction temperature, the conversion of 1-propanol gradually increases from 8% to 12% on the increase of reaction temperature from 200°C to 250°C. When the reaction temperature is higher than 250°C the 1-propanol conversion rapidly rises to 80% at 400°C and then slightly increases up to 85% at 500°C.

At low 1-propanol conversion the main oxidation product is propionaldehyde with small amounts of CO$_2$ and propylene. At high 1-propanol conversion (above 250°C) propionaldehyde selectivity rapidly decreases while CO$_2$ and propylene selectivities quickly increase. The selectivity to propylene is higher than in case of 8Co/SiO$_2$ and 8Co/MgO catalysts at all the temperature range. The maximum
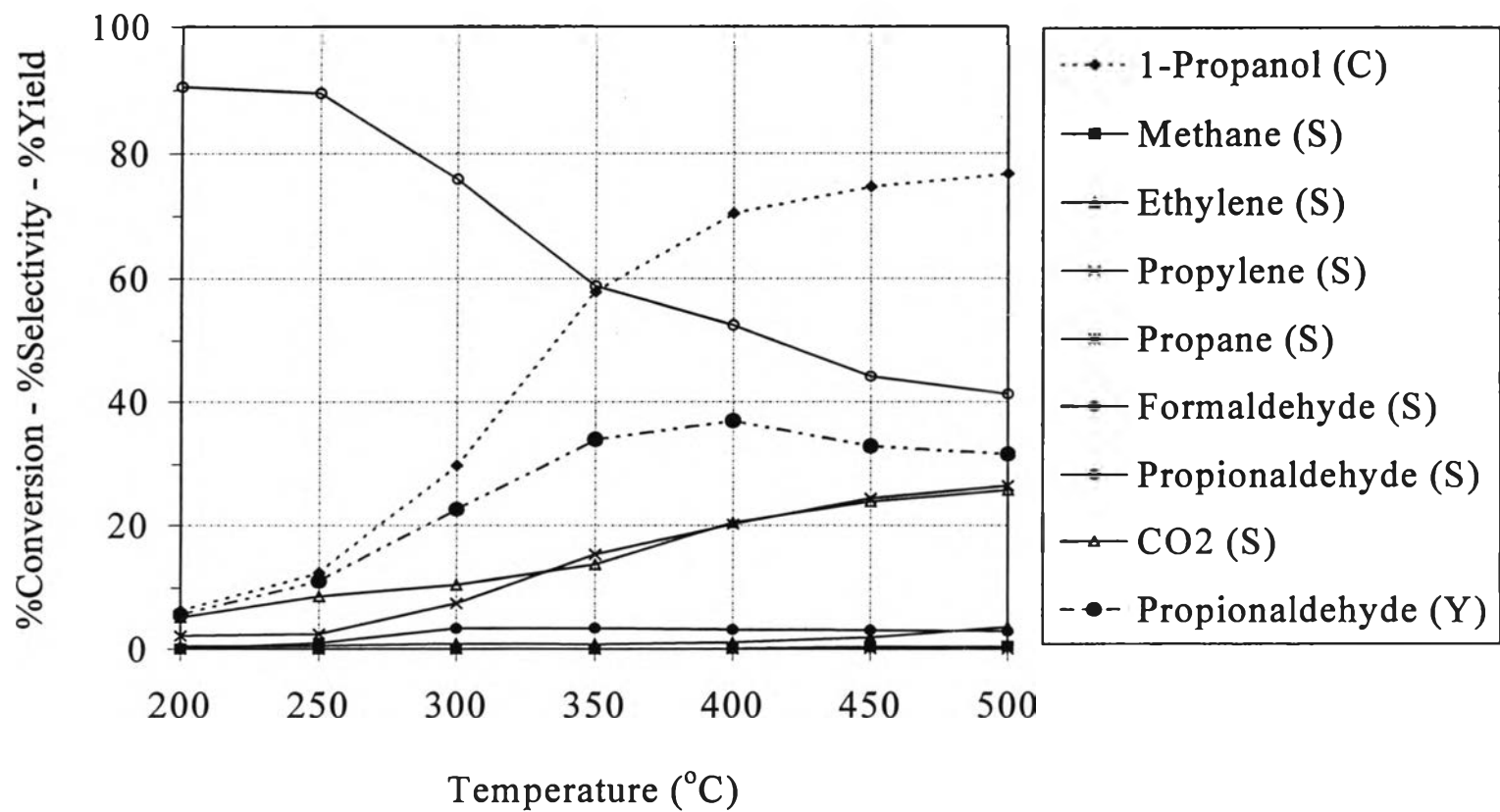
Figure 5.20 Conversion (C) of 1-propanol, product selectivities (S), and yield (Y) of propionaldehyde on 8Co/SiO₂ catalyst in the 1-propanol oxidation.

selectivities to CO_2 and propylene are about 25% and 41% at 500°C and the maximum yield of propionaldehyde is ca. 34% at 350°C.

From the results of 1-propanol oxidation that are shown above, it suggests that 8Co/MgO catalyst gives the highest propionaldehyde yield ca.53% at 400°C when compared with other catalysts.

5.2.4 2-Propanol oxidation

- **8Co/MgO catalyst**

The behavior of 8Co/MgO as a catalyst for 2-propanol oxidation is described in figure 5.22. Increasing the reaction temperature from 200°C to 400°C results in the increase in 2-propanol conversion from 15% to 61%. Further increasing temperature above 400°C hardly affects the conversion of 8Co/MgO catalyst that seems to reach a steady value of approximately 58%. CO_2 selectivity moderately enhances from 9% to 42% at reaction temperature range 250-500°C. Traces of methane, ethylene, and propane are detected at all reaction temperature range.

- **8Co/SiO₂ catalyst**

Figure 5.23 shows the catalytic property of 8Co/SiO₂ catalyst for 2-propanol oxidation. At low reaction temperature (200-300°C) the activity of 8Co/SiO₂ catalyst steadily increases from 14% to 26% 2-propanol conversion on the increase of temperature from 200-300°C. The conversion of 2-propanol significantly rises up from 26% to 66% in the temperature range 300-400°C. Above 400°C, the 2-propanol conversion slightly increases and levels off at 69% at 500°C.

At low 2-propanol conversion (200-300°C) the major reaction product is propylene and trace of CO_2 whereas at high 2-propanol conversion propylene and CO_2 are the main products and there are some formation of other by-products i.e. methane, ethylene, and propane. At high 2-propanol conversion (300-500°C) the

selectivity of propylene steadily goes down and levels off at about 56% while the selectivity of CO_2 steadily increases to 40%.

- **8Co/γ-Al$_2$O$_3$ catalyst**

The catalytic activity of 8Co/γ-Al$_2$O$_3$ catalyst is illustrated in figure 5.24. The conversion of 2-propanol rapidly increases from 28% to 76% at the reaction temperature range 200-350°C. When increase the reaction temperature to 500°C, the 2-propanol conversion is rather constant at about 78%.

At the initial reaction temperature (200-300°C) the main product is propylene and trace of CO_2 whereas at high reaction temperature (300-500°C) the main products are propylene and CO_2. The selectivity to propylene steadily decreases from 96% to 58% while the selectivity to CO_2 increases from 3% to 40% in the temperature range 300-500°C.

From the above results, it is found that the activity of all catalysts has the same trend. The selectivity to CO_2 increases when the reaction temperature rises but the main reaction product is still propylene at all reaction temperature and 8Co/γ-Al$_2$O$_3$ catalyst exhibits the highest propylene selectivity.

5.2.5 1-Butanol oxidation

- **8Co/MgO catalyst**

Figure 5.25 shows the activity and selectivity of 8Co/MgO catalyst. The activity increases at the beginning (200-250°C) and increases very rapidly to 91% and then slightly rises up to 96% at 500°C. At all the reaction temperature range, CO_2 is the main product and there are some formations of methane ethylene, propane, propylene, and formaldehyde. The selectivity to CO_2 is in the range 70-90% over the whole reaction temperature.
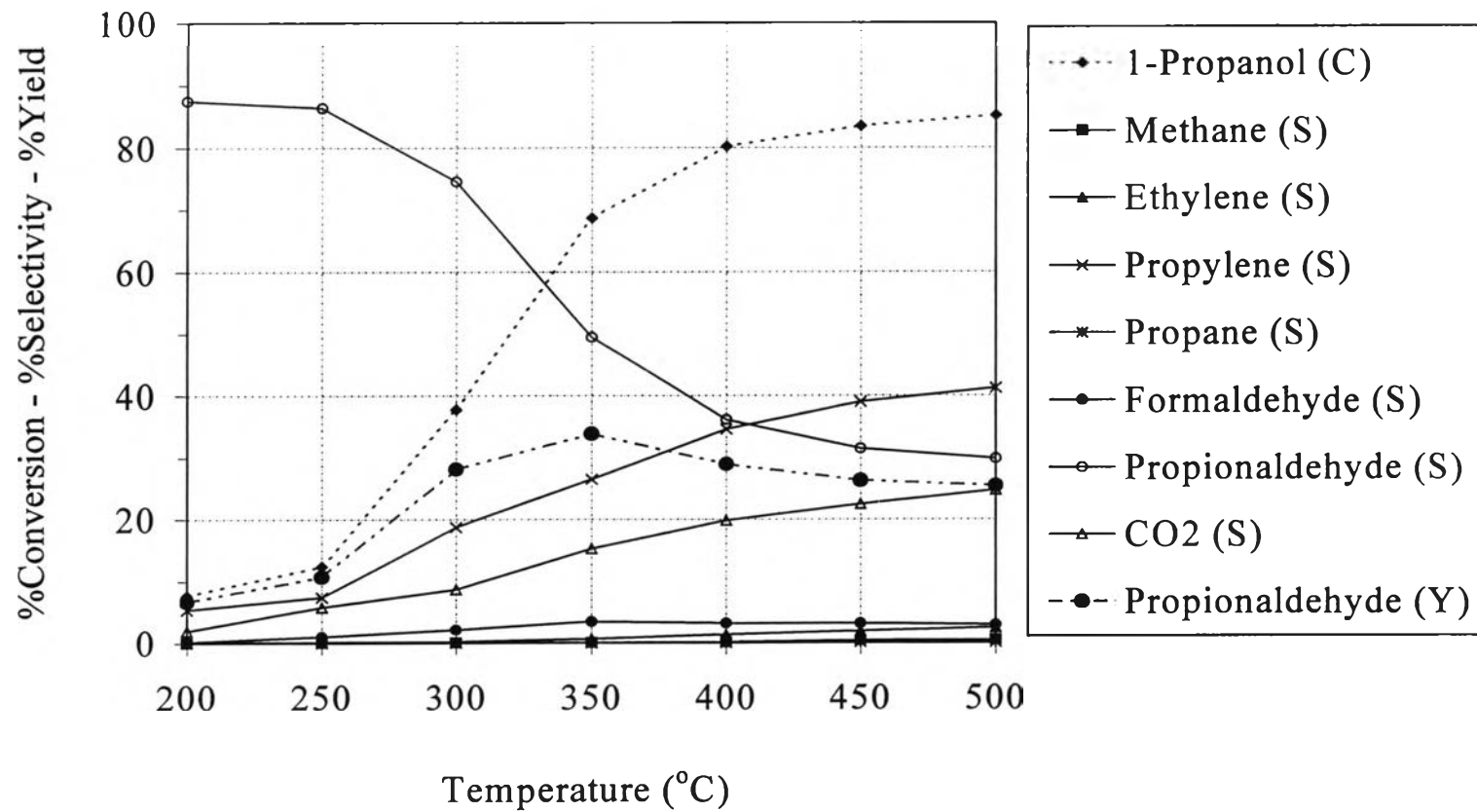
Figure 5.21 Conversion (C) of 1-propanol, product selectivities (S), and yield (Y) of propionaldehyde on $8Co/\gamma-Al_2O_3$ catalyst in the 1-propanol oxidation.
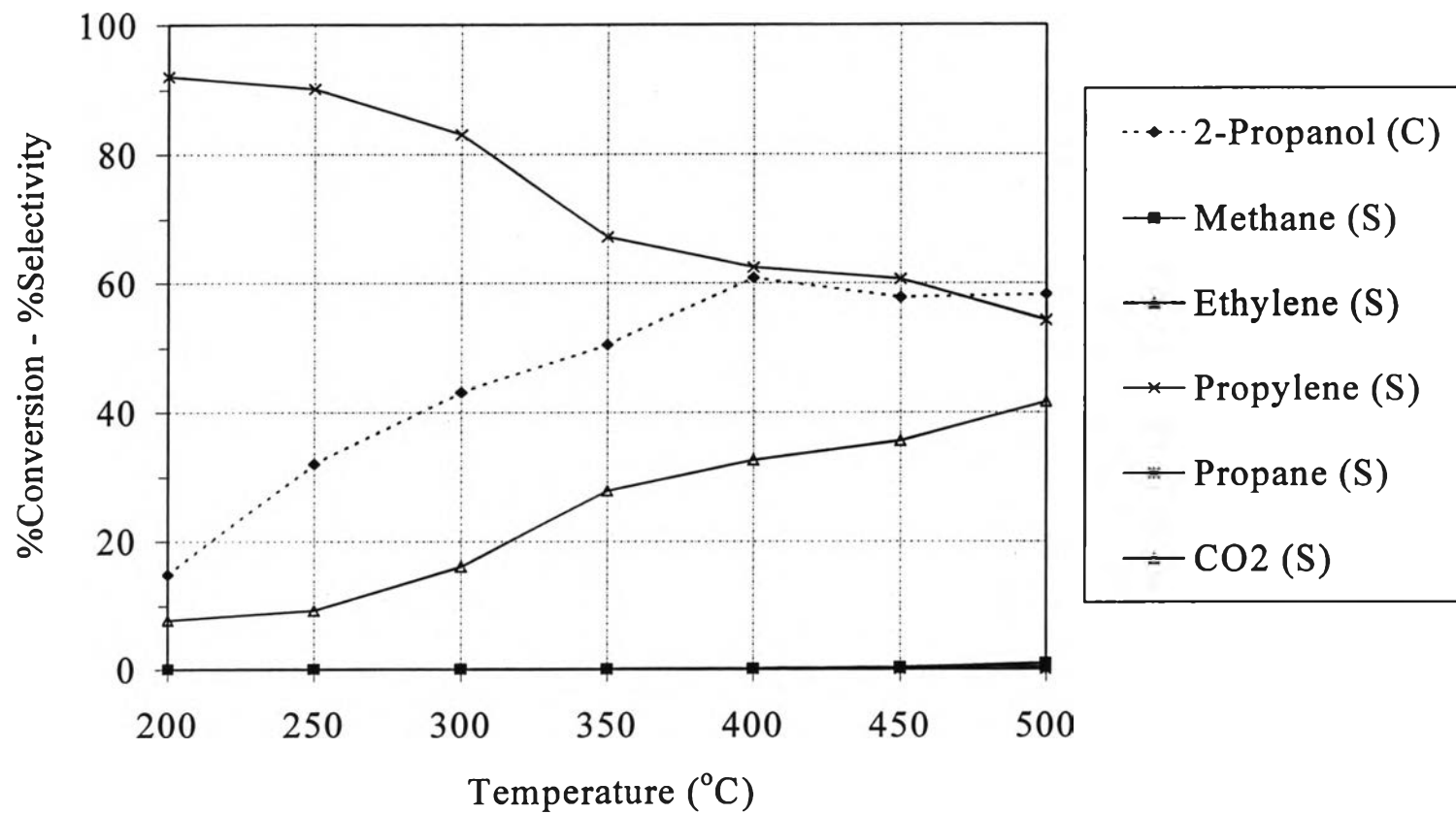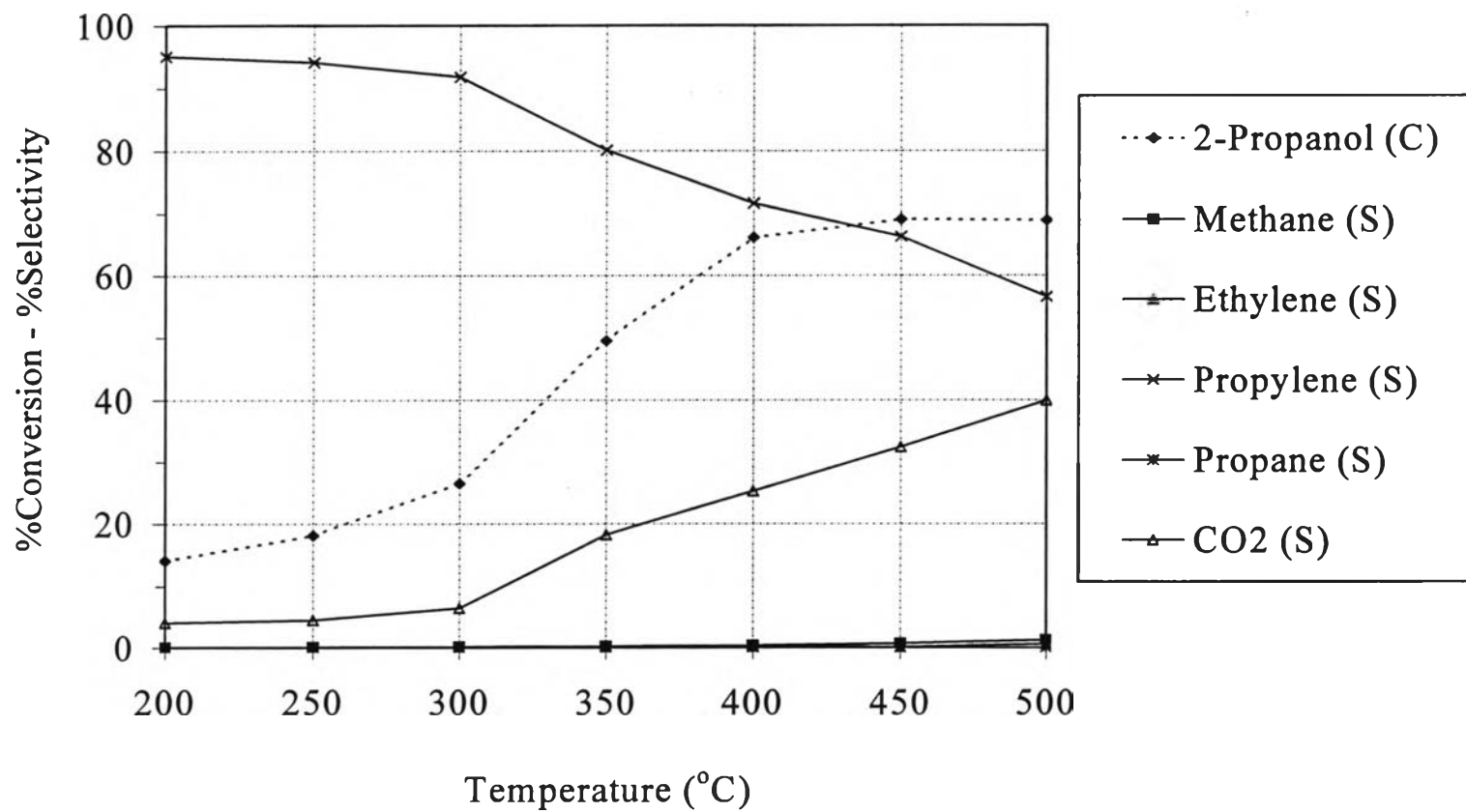
Figure 5.22 Conversion (C) of 2-propanol and product selectivities (S) on 8Co/MgO catalyst in the 2-propanol oxidation.

Figure 5.23 Conversion (C) of 2-propanol and product selectivities (S) on 8Co/SiO$_2$ catalyst in the 2-propanol oxidation.
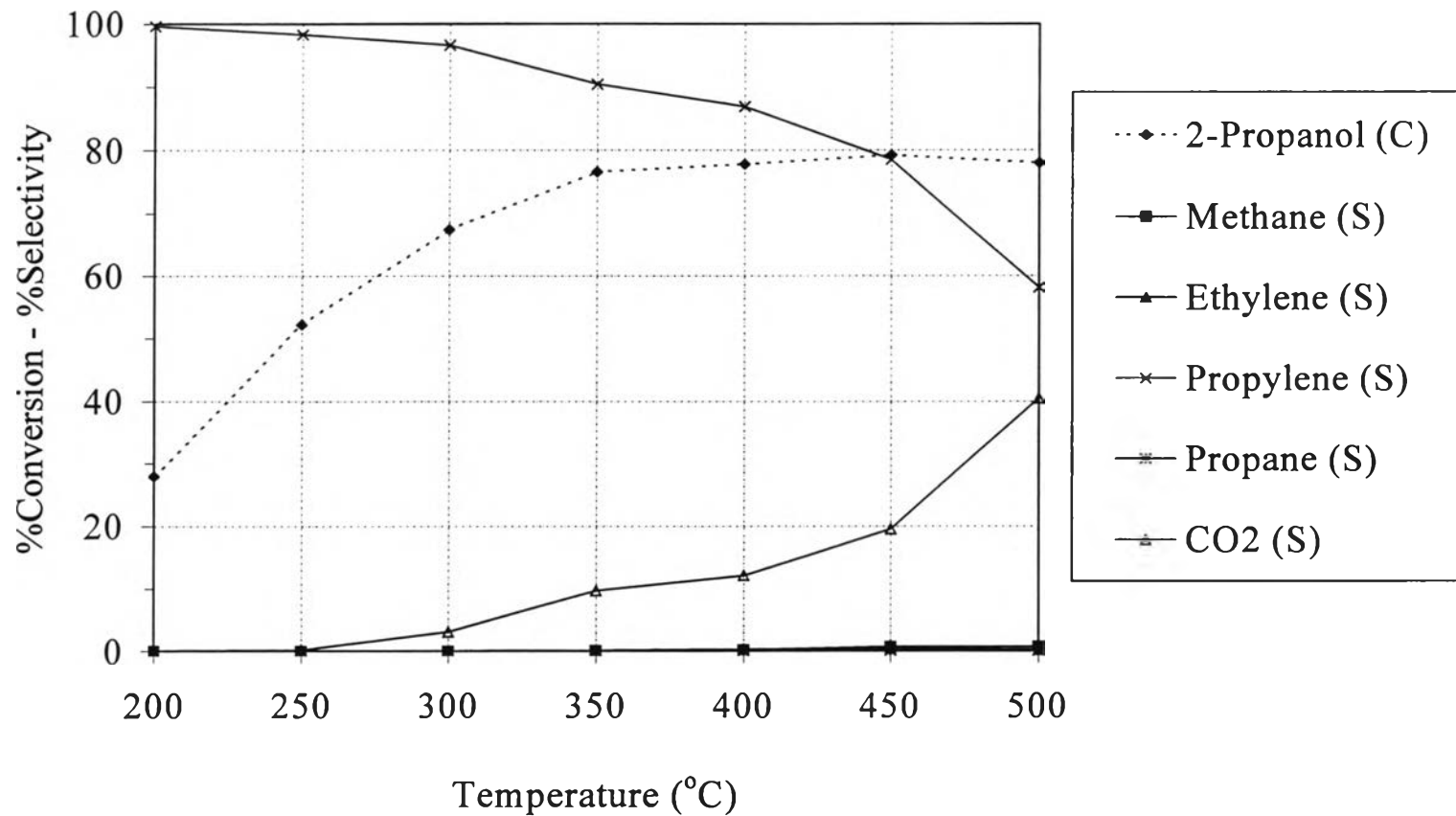
Figure 5.24 Conversion (C) of 2-propanol and product selectivities (S) on 8Co/γ-Al$_2$O$_3$ catalyst in the 2-propanol oxidation.
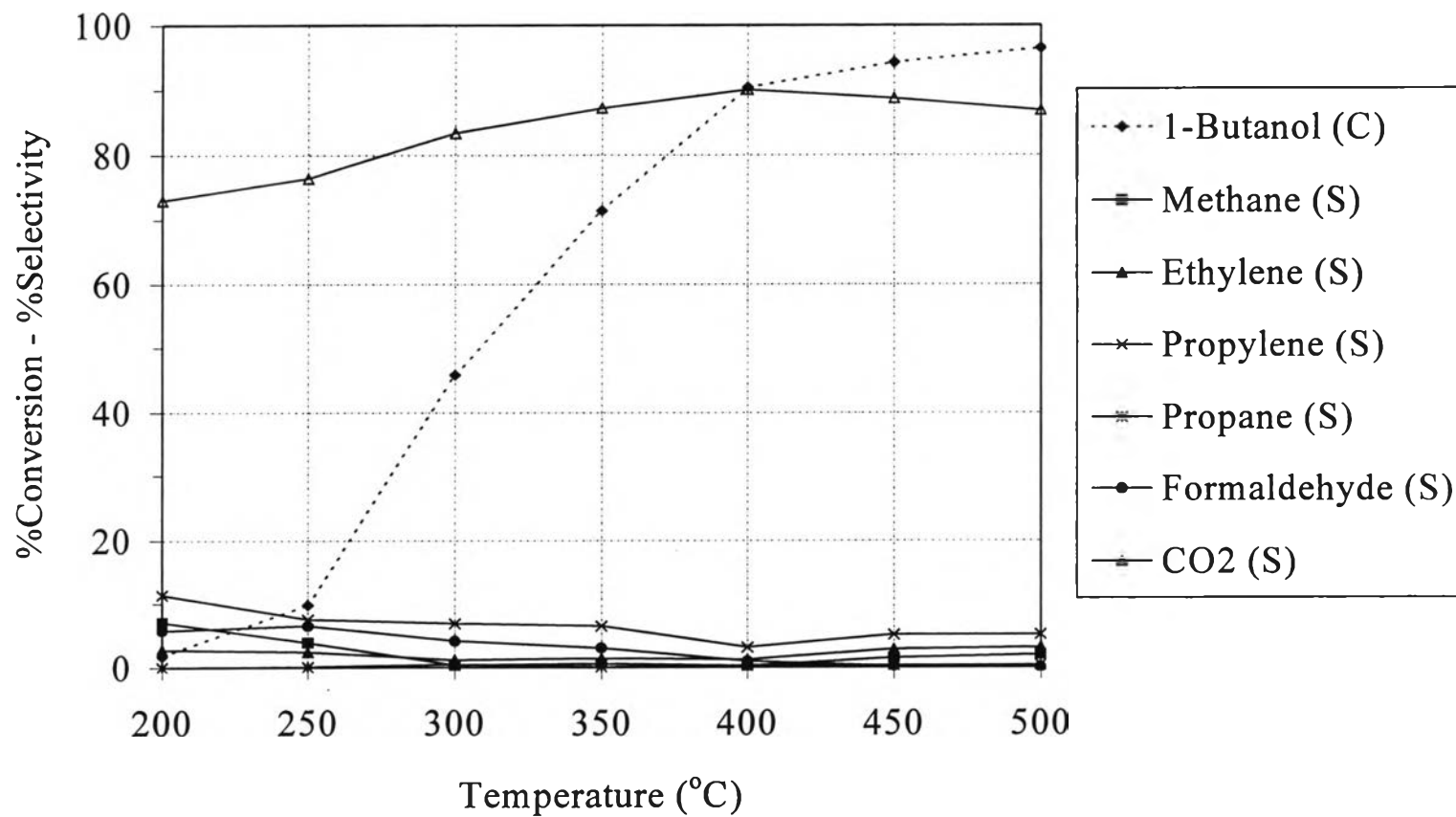
Figure 5.25 Conversion (C) of 1-butanol and product selectivities (S) on 8Co/MgO catalyst in the 1-butanol oxidation.

- **8Co/SiO$_2$ catalyst**

The result of catalytic test on 8Co/SiO$_2$ catalyst is shown in figure 5.26. 1-butanol conversion steadily increases from 16% to 98% at the reaction temperature range 200-350°C. Above 350°C, the conversion of 1-butanol rises up to 100% at 400°C and keeps constant. The CO$_2$ selectivity slightly enhances from 80% to 92% at 500°C. Small amounts of the reaction by-products i.e. methane, ethylene, propane, propylene, and formaldehyde are detected at all reaction temperature.

- **8Co/γ-Al$_2$O$_3$ catalyst**

Figure 5.27 illustrates the catalytic activity of 8Co/γ-Al$_2$O$_3$ catalyst on 1-butanol oxidation. The conversion of 1-butanol increases from 14% to 97% in the temperature range 200-350°C. Beyond 350°C, the gradual increase of 1-butanol conversion becomes 100% at 400°C. At all the reaction temperature range, CO$_2$ is the main product and there are some formation of methane, ethylene, propane, propylene, and formaldehyde. When the reaction temperature rises to 500°C, the selectivity to CO$_2$ goes up to 91% while the selectivity to by-products and propylene gradually declines.

From the data of 1-butanol oxidation reaction, it can be illustrated that all catalysts give almost the same conversion pattern. 1-Butanol is decomposed to CO$_2$ and some of methane, ethylene, propane, propylene, and formaldehyde.

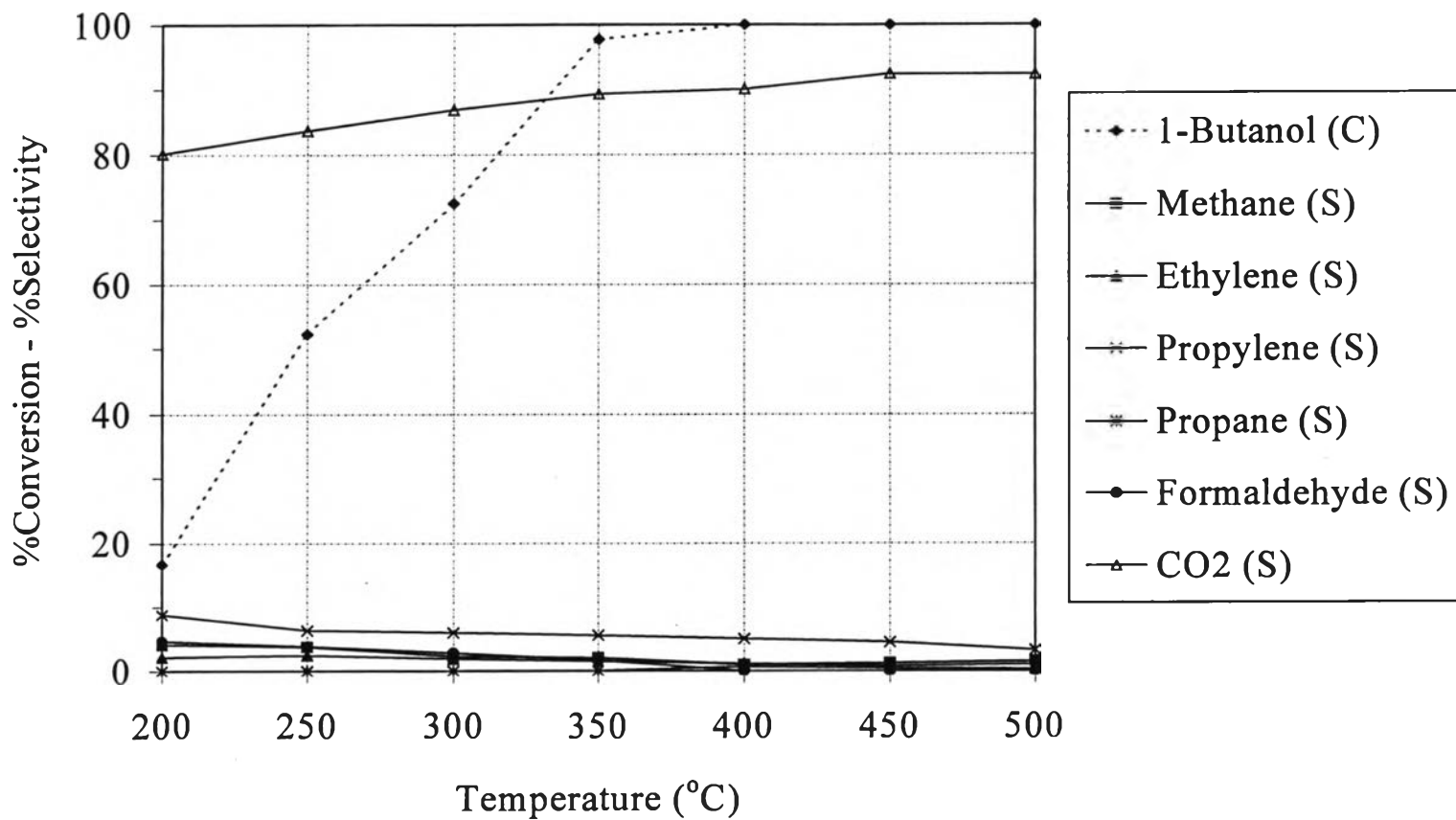**Figure 5.26** Conversion (C) of 1-butanol and product selectivities (S) on 8Co/SiO₂ catalyst in the 1-butanol oxidation.
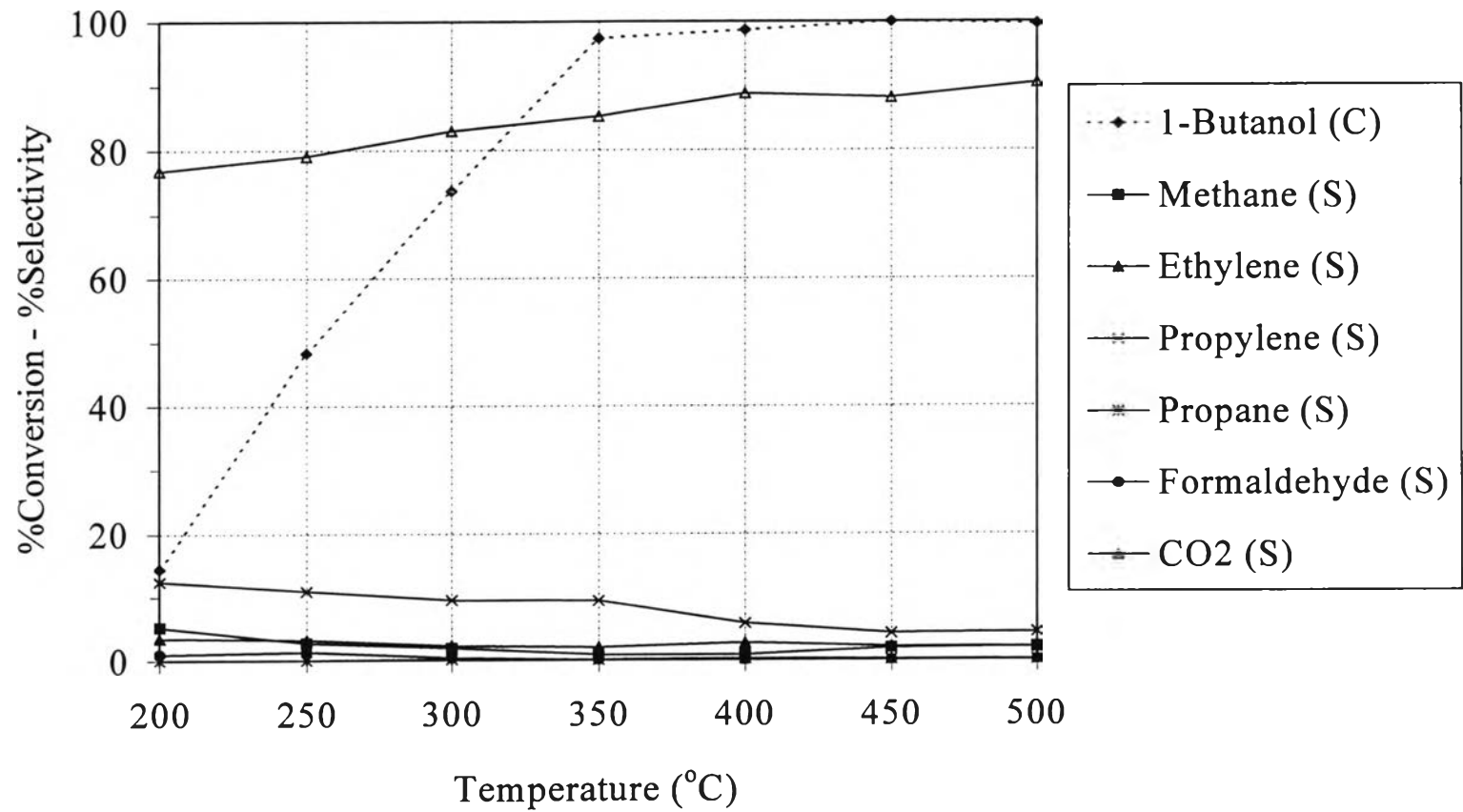
Figure 5.27 Conversion (C) of 1-butanol and product selectivities (S) on 8Co/γ-Al₂O₃ catalyst in the 1-butanol oxidation.

5.2.6 Effect of support on cobalt oxide catalyst

From the FT-IR data, 8Co/MgO catalyst exhibits the same IR spectra as MgO support. These results suggest that in these regions, the absorption band of MgO may hide the IR spectra of cobalt oxide or there is no cobalt oxide form in 8Co/MgO catalyst. Since the XRD results do not indicate any cobalt oxide structure, the cobalt in 8Co/MgO catalyst may form the microcrystalline state or thin layer so that the XRD technique can not detect.

To investigate the oxidation property of 8Co/MgO catalyst, methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol are used as reactants on oxidation reaction. From the results of the oxidation reactions, 8Co/MgO catalyst shows the highest catalytic performance for the oxidation of ethanol to acetaldehyde and 1-propanol to propionaldehyde. 8Co/MgO catalyst gives the highest acetaldehyde selectivity (58%) for ethanol oxidation and the highest propionaldehyde selectivity (53%) for 1-propanol oxidation at 400°C.

It is also found that the catalytic property of the catalyst depends on type of support. 8Co/MgO catalyst gives the highest aldehyde yield while 8Co/γ-Al$_2$O$_3$ catalyst provides the lowest aldehyde yield at the same reaction condition. These results can be explained by the acid-base properties of catalyst. The basic property of support falls in the order: MgO > SiO$_2$ > γ-Al$_2$O$_3$. From the previous studies, it has been reported that the dehydrogenation reaction takes place at the basic sites while the dehydration reaction takes place at the acid sites of the catalyst [Kitayama et al. (1996)]. Moreover, it has also been reported that acidity can promote the dehydration reaction of alcohol to olefin and basicity can promote the dehydrogenation reaction of alcohol to oxygenate product [Murthy et al. (1994) and Fishel et al. (1994)]. That is the reason why 8Co/MgO catalyst gives the aldehyde yield higher than 8Co/SiO$_2$ and 8Co/γ-Al$_2$O$_3$ catalysts. The aldehyde yield decreases in the order: 8Co/MgO > 8Co/SiO$_2$ > 8Co/γ-Al$_2$O$_3$ catalyst.

For 2-propanol oxidation reaction, All catalysts provide high propylene selectivity. However, $8Co/\gamma-Al_2O_3$ catalyst gives the highest propylene selectivity at all reaction temperature range. It can be seen that almost all 2-propanol is dehydrated to propylene. While in case of 1-propanol oxidation, the selectivity to propylene is lower than on 2-propanol oxidation when using the same catalyst and the same reaction condition. It can be explained that the ease of dehydration of alcohol decreases in the order: tertiary > secondary > primary alcohol. Therefore, 2-propanol is dehydrated easier than 1-propanol, and then gives the higher selectivity to propylene. Furthermore, the nature of support also affects to the selectivity to propylene. The propylene selectivity declines in the order: $8Co/\gamma-Al_2O_3$ > $8Co/SiO_2$ > $8Co/\gamma-Al_2O_3$ catalyst. The data is consistent with previous studies that when the Al content of the Mg-Al mixed oxide increased, the turnover rate for 2-propanol dehydration increased [Fishel *et al.* (1994)].

In case of methanol and 2-butanol oxidation reaction, $8Co/MgO$ catalyst is very active for the oxidation of methanol and 1-butanol but nonselective for selective oxidation product. However, $8Co/MgO$ catalyst plays roles as combustion catalyst due to the fact that methanol and 1-butanol are mostly convert to CO_2 and water. In these cases, the property of support has little effect to the catalytic activity on methanol and 1-butanol oxidation.

It is known that acidity can promote bond cleavage in organic chemicals and produce CO_2. Therefore, $8Co/\gamma-Al_2O_3$ catalyst gives higher CO_2 selectivity than $8Co/SiO_2$ and $8Co/MgO$ catalyst.

All data exhibit that $8Co/SiO_2$ catalyst has the catalytic behavior close to $8Co/\gamma-Al_2O_3$ catalyst. It is consistent with the literature that cobalt species presented on the surface of SiO_2 and $\gamma-Al_2O_3$ is Co_3O_4 [Novochinsky *et al.* (1998)]. It is known that cobalt oxide, Al, and Si have amphoteric property while Mg has basic property. Therefore, the interaction between cobalt oxide with Si and Al is weaker than in case of cobalt oxide and Mg. Therefore, Co and MgO is likely to form new Co-Mg-O

compound, hence, 8Co/MgO has the catalytic behavior differ from 8Co/SiO$_2$ and 8Co/γ-Al$_2$O$_3$ catalysts.

5.2.7 Reaction mechanism

From the results of 1-propanol and 2-propanol oxidation reactions, it can be seen that the main product of these two reactions is different. Propionaldehyde is the major product for 1-propanol oxidation while propylene is the main product for 2-propanol oxidation. For V-Mg-O catalyst, it was found that there were formations of V-O-V site at the surface of the catalyst [Bettasar et al. (1996)]. Therefore, it may be possible to postulate that there are some formations of Co-O-Co site at the surface of Co-Mg-O catalyst. The following reaction mechanisms are proposed to explain the phenomena of the catalyst:
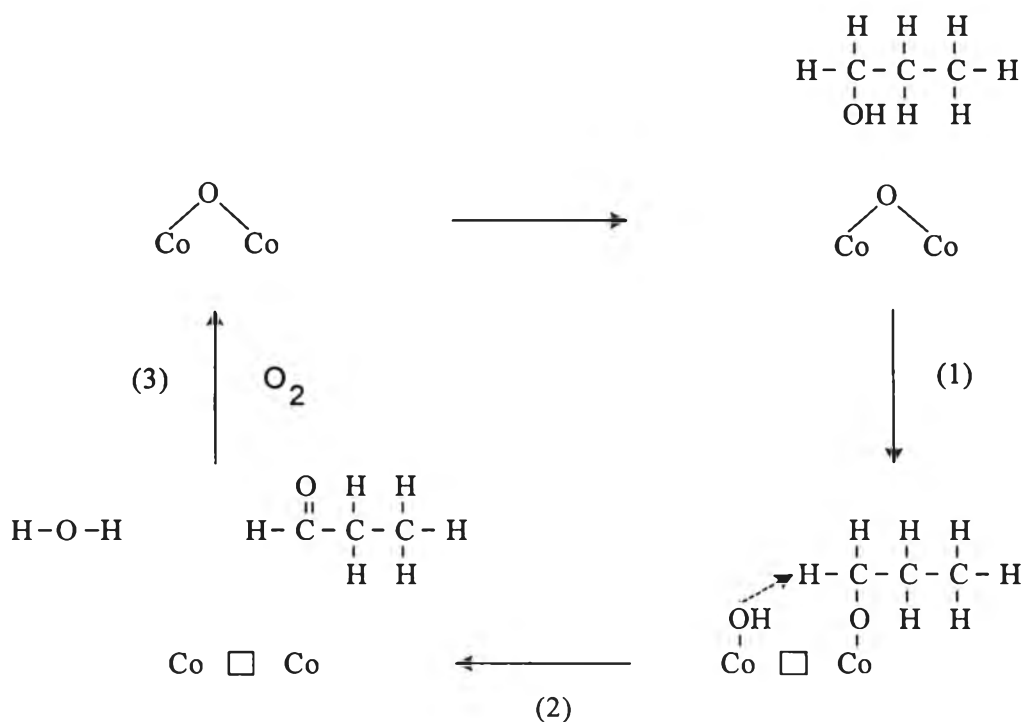

Figure 5.28 The mechanism of the oxidation of 1-propanol to propionaldehyde
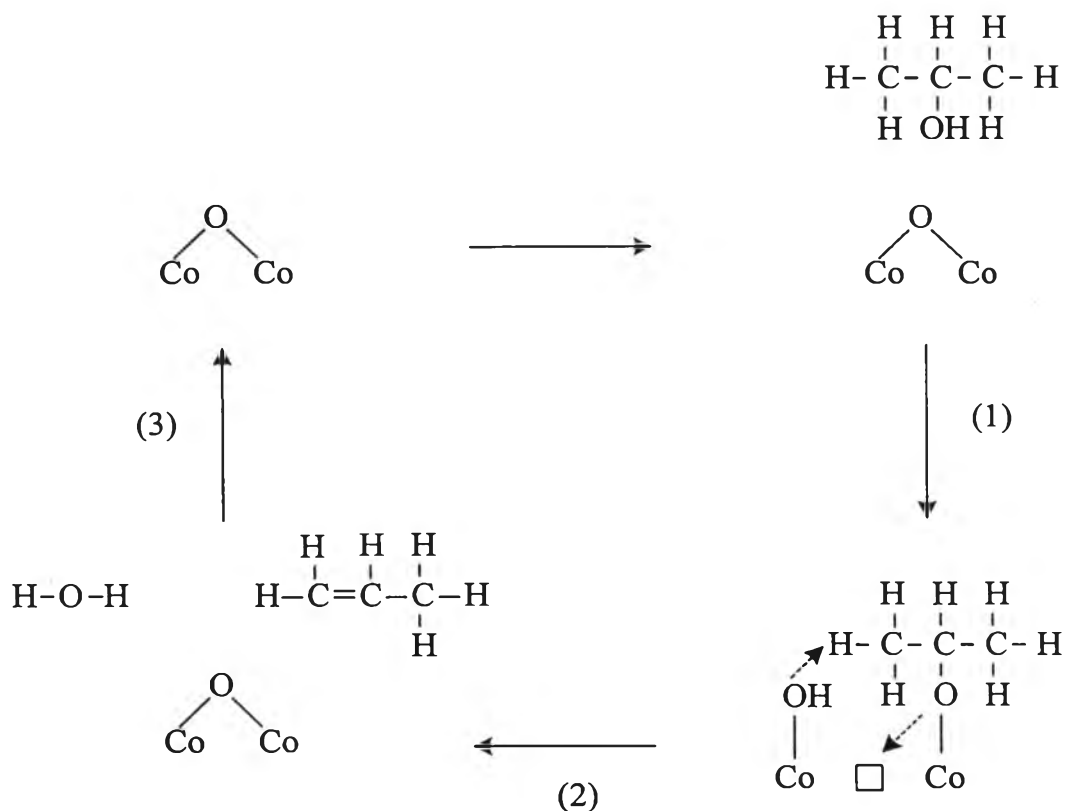
H H H
H- C- C- C- H
H OH H

O
Co Co

⟶

O
Co Co

(3)

(1)

H-O-H

H H H
H–C=C–C–H
H

O
Co Co

H H H
H- C- C- C- H
OH H O H

Co □ Co

(2)

Figure 5.29 The mechanism of the oxidation of 2-propanol to propylene

The oxidation mechanism of 1-propanol is shown in figure 5.28. 1-Propanol is adsorbed on Co-O-Co site to produce adsorbed alkoxide species. H-atom of the alcohol hydroxyl group is subtracted in the form of hydroxyl group by O anion on the catalyst surface. The surface hydroxyl group further subtracted H of the C atom alcohol to O atom to form water and aldehyde product. Desorption of water causes vacant oxygen in Co-□-Co site on the catalyst surface. Finally, Co-□-Co site is reoxidized by the oxygen from the gas phase to form Co-O-Co site again.

For the mechanism as shown in figure 5.29, 2-propanol via hydroxyl group is adsorbed on Co-O-Co site to produce adsorbed alkoxide species and hydroxyl group on the surface of catalyst. Then, H atom from the adsorbed alkoxide species is subtracted by the hydroxyl group to form water and propylene concurrent with the return to Co-O-Co site.

From the mechanisms exhibited in figures 5.28 and 5.29, it may be explained that propionaldehyde is occurred by breaking the C-H bond of 1-propanol whereas propylene is found by breaking the C-O bond of 2-propanol. It is also shown that these two mechanisms occur competitively and mechanism in the figure 5.28 is preferably occurred as the alcohol is changed from primary to secondary to tertiary. That is the reasons why 1-propanol and 2-propanol provide different major product at the same reaction condition.