

CHAPTER V

RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two parts, the characterization of Co-Mg-O catalysts and the catalytic oxidation reaction of propane, 1-propanol, propene, and CO, respectively.

5.1 Catalyst characterization

5.1.1 Determination of metal content of catalyst and BET surface area.

The results of metal composition and surface area of Co-Mg-O catalyst which are analyzed by Atomic Absorption Spectroscopy (AAS) and BET surface area are summarized in Table 5.1.

Table 5.1 The metal composition and BET surface area of Co-Mg-O catalysts.

Catalyst	%Cobalt content	BET surface area (m ² /g)
MgO	-	40
4Co-Mg-O	3.7	54
8Co-Mg-O	7.6	65
12Co-Mg-O	11.6	78

The data in Table 5.1 show that the cobalt content in Co-Mg-O sample is near the value calculated and the surface area of Co-Mg-O catalyst steadily increases with increasing cobalt loading.

5.1.2 Fourier Transform Infrared Spectrometer (FT-IR)

The IR spectrum is used to identify the functional group on the Co-Mg-O surface. The infrared radiation is used in the wavelength of $400 - 2000 \text{ cm}^{-1}$.

The IR spectra of Co-Mg-O catalysts are showed in figures 5.1 – 5.4. Figure 5.1 shows the IR spectrum of MgO support. The IR absorption bands are measured in the region $400-800$, 880 , 1130 , and 1480 cm^{-1} . Figure 5.2 presents the IR spectrum of 4Co-Mg-O catalyst which give the same IR spectrum as detect on MgO. The absorption peaks of 8Co-Mg-O (figure 5.3) detected in the region $400-800$, 880 , 1130 , and 1480 cm^{-1} also exhibits the same pattern as MgO. In figure 5.4 the IR spectrum of 12Co-Mg-O still does not show the presence of cobalt oxide but MgO support. 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 Co-Mg-O catalyst is not measurable because in these regions the IR spectra of cobalt oxide may be hidden by the absorption of MgO.



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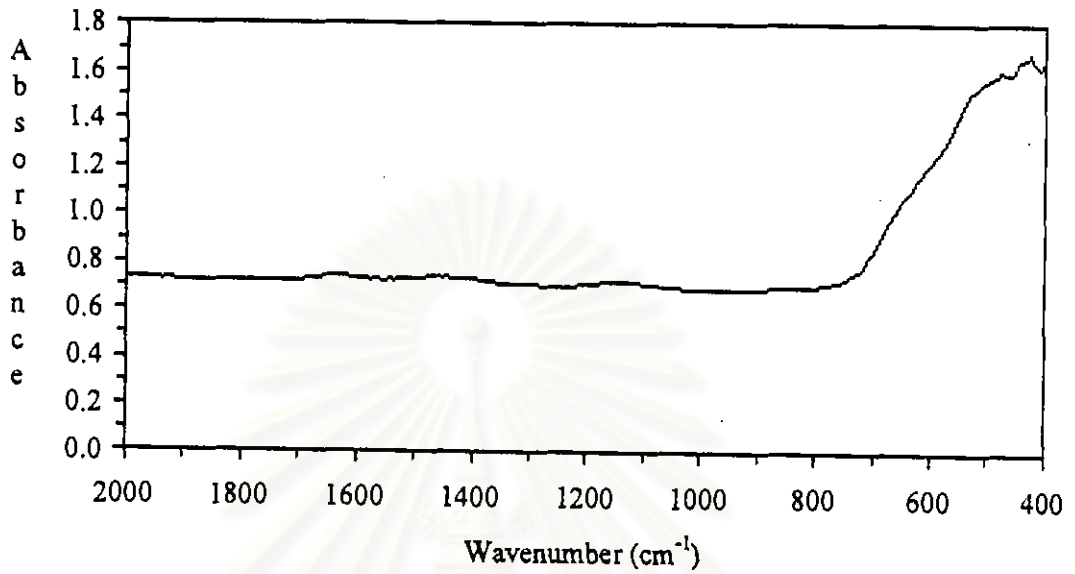


Figure 5.1 IR spectrum of MgO catalyst.

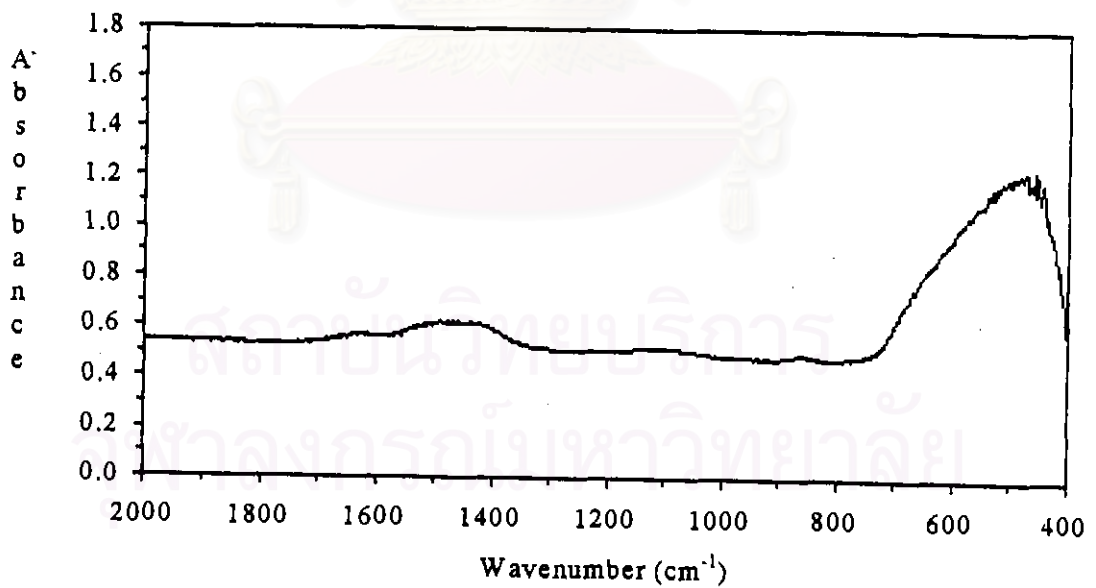


Figure 5.2 IR spectrum of 4Co-Mg-O catalyst.

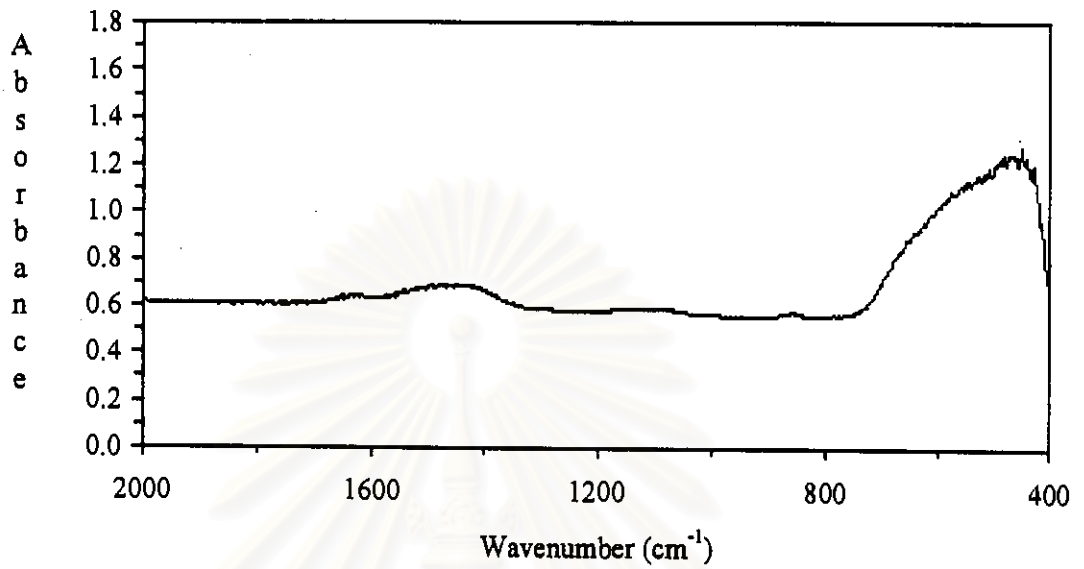


Figure 5.3 IR spectrum of 8Co-Mg-O catalyst.

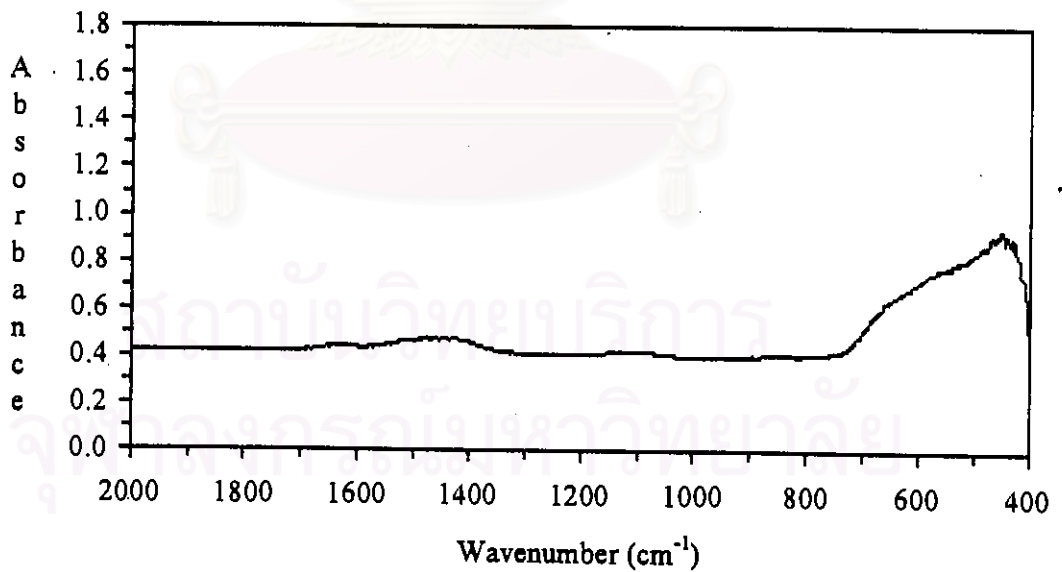


Figure 5.4 IR spectrum of 12Co-Mg-O catalyst.

5.1.3 X-Ray Diffraction (XRD)

The crystal structure of catalyst is identified by X-ray Diffraction technique. Figures 5.5 - 5.8 reveal the results of XRD spectra of Co-Mg-O catalysts (MgO, 4Co-Mg-O, 8Co-Mg-O, and 12Co-Mg-O catalysts).

The XRD pattern of MgO catalyst is presented in figure 5.5. The XRD pattern of MgO catalyst shows 5 peaks at 36.5° , 43° , 62° , 75° , and 78° . As present in figure 5.6, the XRD pattern of 4Co-Mg-O catalyst shows only the peaks of MgO support. However, the intensity of the XRD peak of 4Co-Mg-O is lower than MgO peaks. Figure 5.7 shows that for 8Co-Mg-O catalyst the XRD peaks is the same as MgO but the level of intensity is lower than MgO and 4Co-Mg-O catalysts. For 12Co-Mg-O catalyst (figure 5.8), the XRD can detect only the peaks of MgO but the level of intensity is lower than MgO, 4Co-Mg-O, and 8Co-Mg-O catalysts.

From the XRD results that 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 Co-Mg-O catalyst forms a thin layer of some Co-Mg-O compounds distribute on the surface of catalyst that XRD diffraction can not measure. The structure of Co-Mg-O catalysts are similar to MgO, but more amorphous.

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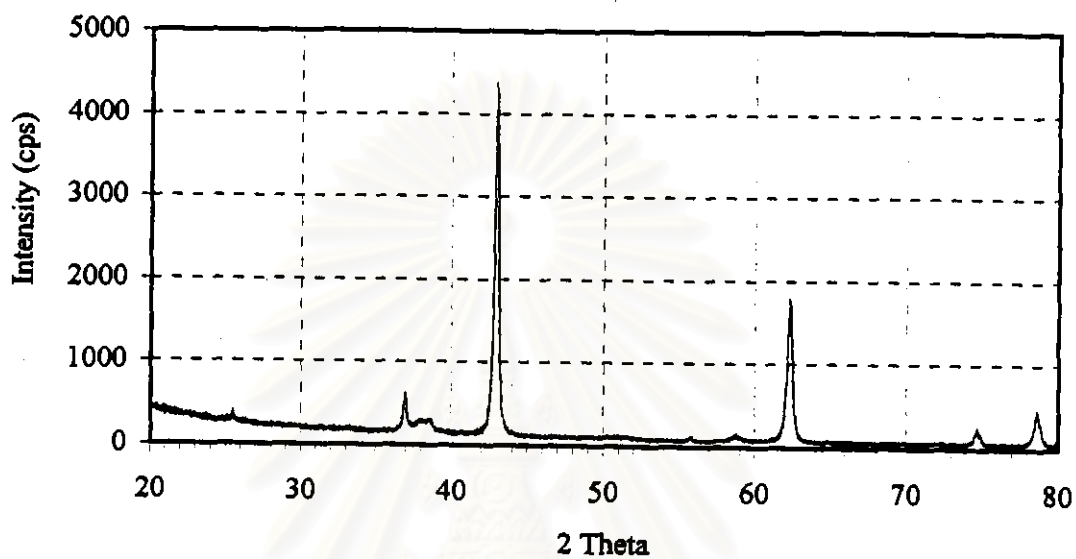


Figure 5.5 The XRD pattern of MgO catalyst.

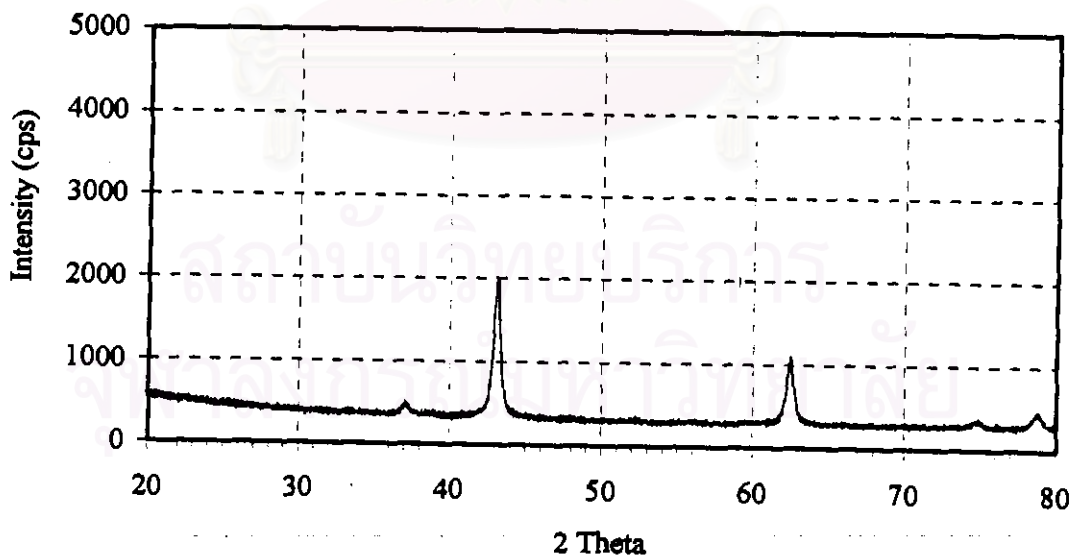


Figure 5.6 The XRD pattern of 4Co-Mg-O catalyst.

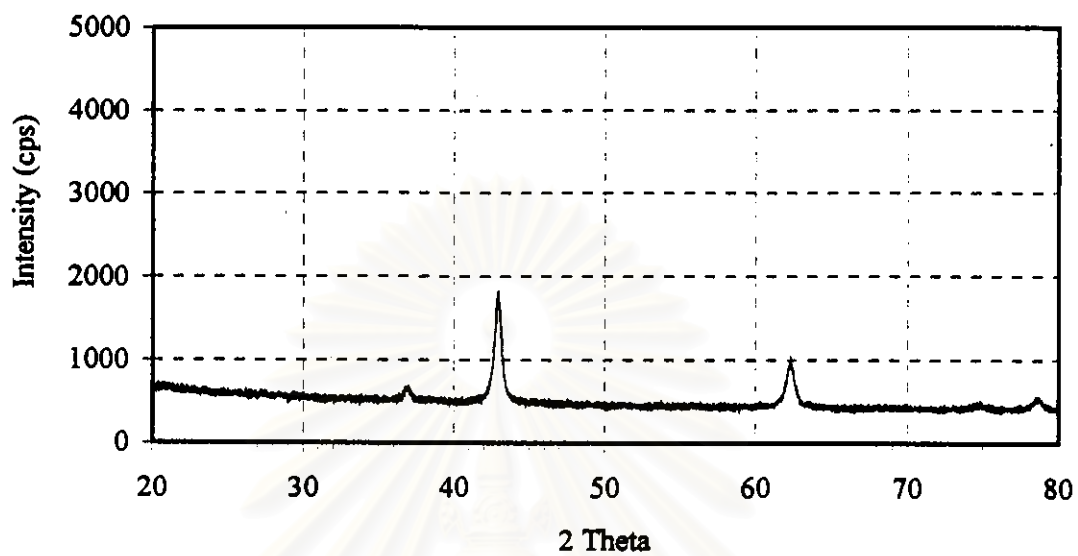


Figure 5.7 The XRD pattern of 8Co-Mg-O catalyst.

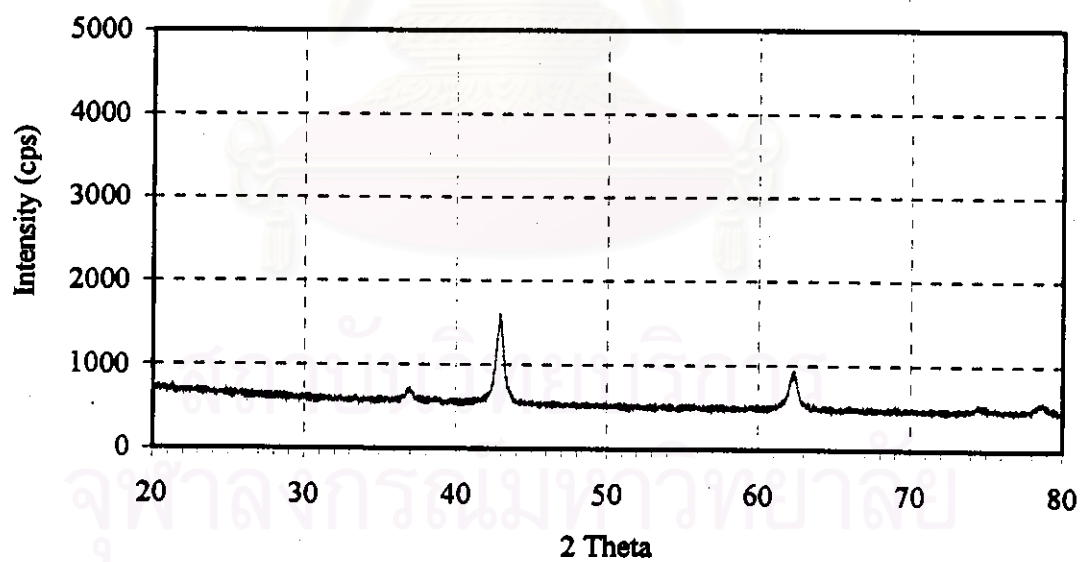


Figure 5.8 The XRD pattern of 12Co-Mg-O catalyst.

5.1.4 Temperature programmed reduction (TPR)

The TPR profiles of Co-Mg-O catalysts are given in figures 5.9-5.12. The TPR curves is measured between 50-700°C. The area under each curve shows the oxygen content on each oxide catalyst. The slope of the TPR curve in each catalyst indicates the tendency of amount of oxygen reduced by hydrogen. At low reduction temperature, the trend of TPR profile slightly rises when the reduction temperature increases due to the drift of electric signal. However, at high reduction temperature the signal from the reduction on the oxide catalyst is so high that the drift of electric signal can be neglected.

Figure 5.9 demonstrates the TPR profile of 4Co-Mg-O catalyst. The TPR profile shows only one reduction peak at around 600°C. In the temperature range about 50-450°C, the slope of TPR profile of 4Co-Mg-O catalyst slightly increases with increasing reduction temperature. However, when the temperature is above 450°C, the slope of TPR profile significantly rises when the reduction temperature increases from 450°C to 700°C. This means that beyond 450°C, a large amount of oxides on the surface of catalyst is reduced by hydrogen.

The TPR spectrum of 8Co-Mg-O catalyst is shown in figure 5.10. 8Co-Mg-O catalyst has the TPR pattern resembles to 4Co-Mg-O catalyst. There is one TPR peak is observed at high temperature at around 550°C on the 8Co-Mg-O catalyst. Nevertheless, the area under TPR curve of 8Co-Mg-O catalyst is higher than 4Co-Mg-O catalyst. At the low reduction temperature the slope of TPR spectrum slightly increases when the reduction temperature rises from 50°C to 400°C. However, at above 400°C, the slope of TPR pattern significantly increases. This result suggests that when the reduction temperature is higher than 400°C a larger amount of oxide on the surface of 8Co-Mg-O catalyst is reduced.

Figure 5.11 shows the TPR pattern of 12Co-Mg-O catalyst. There is no reduction peak occurs in the temperature range 50-700°C. At low reduction temperature the slope of TPR profile steadily goes up with increasing reduction

temperature while at high reduction temperature (at above 350°C) the slope of TPR profile becomes rapidly rises on the increase of reduction temperature. From the TPR behavior of this catalyst no peak is observed due to the fact that the TPR peak may be noticeable at the temperature higher than 700°C. However, the area under the TPR profile of 12Co-Mg-O is higher than 8Co-Mg-O and 4Co-Mg-O catalyst.

Figure 5.12 demonstrates the result of TPR profile for 4Co-Mg-O, 8Co-Mg-O, and 12Co-Mg-O catalysts. From these data, TPR profile of Co-Mg-O catalyst is changed depending on the cobalt concentration in the Co-Mg-O catalyst. At low reaction temperature the slopes of all catalysts slightly increase with the increasing reduction temperature. Even so, at high reduction temperature the slope of all catalysts rapidly rises when the reduction temperature enhances. However, the change of slope of 12Co-Mg-O catalyst starts at lower reduction temperature than 8Co-Mg-O and 4Co-Mg-O catalysts. The result shows that as the cobalt loading in the catalyst is increased, the change of slope of TPR profile is shift to a lower reduction temperature and the area under TPR profile increases. It means that when the cobalt loading in the catalyst increases the more amount of oxides on the surface of Co-Mg-O catalyst is easy to be reduced at lower reduction temperature.

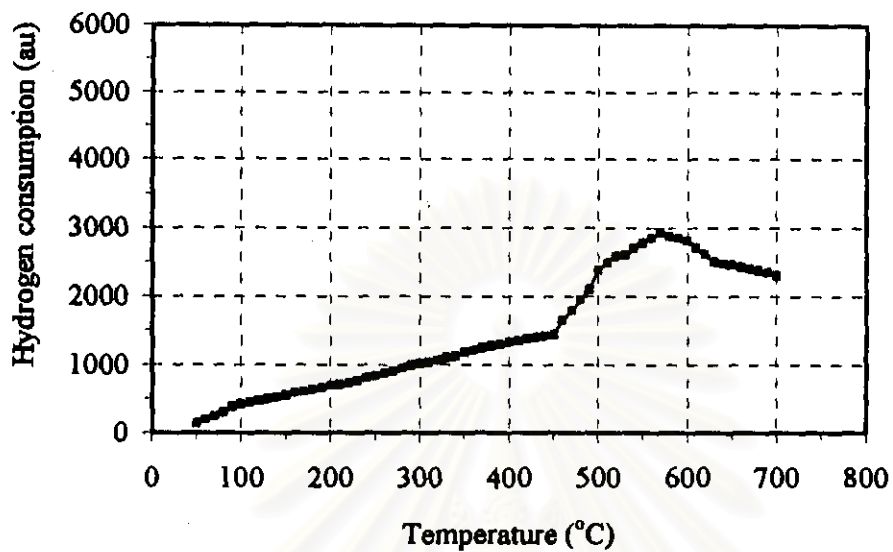


Figure 5.9 The TPR profile of 4Co-Mg-O catalyst.

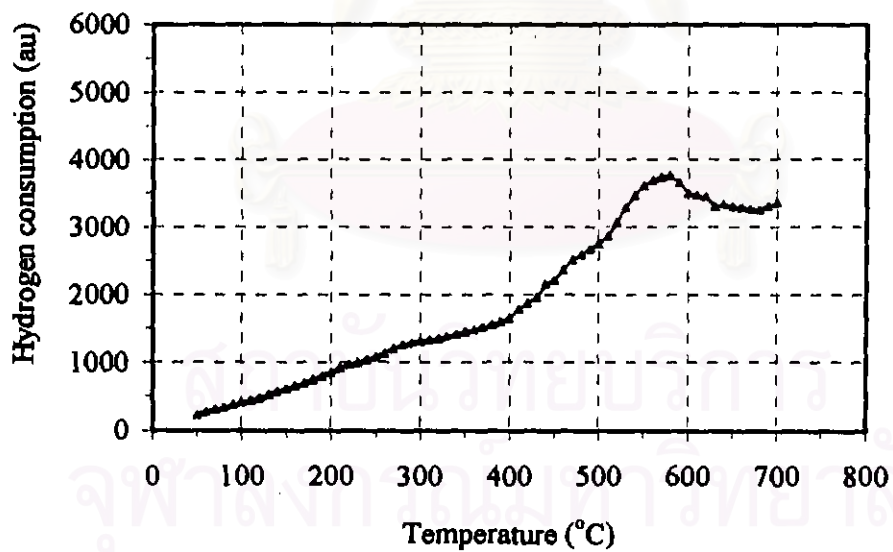


Figure 5.10 The TPR profile of 8Co-Mg-O catalyst.

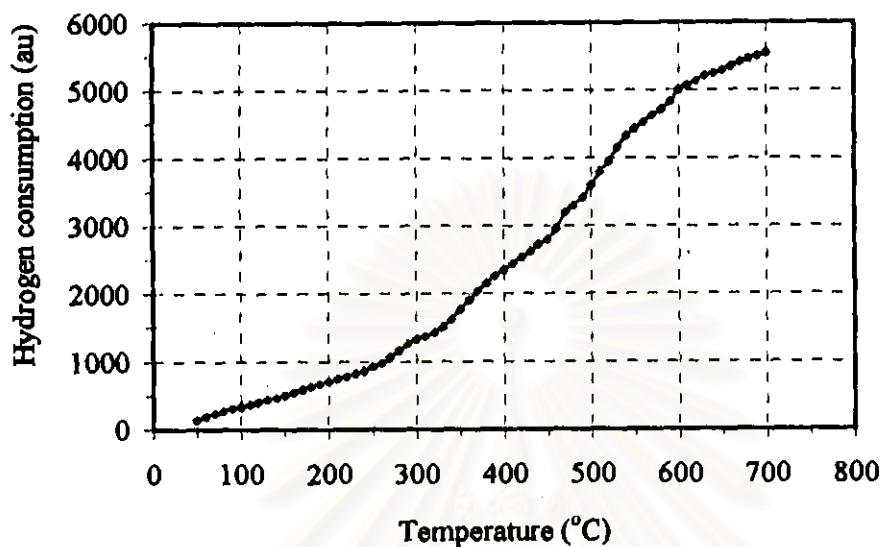


Figure 5.11 The TPR profile of 12Co-Mg-O catalyst.

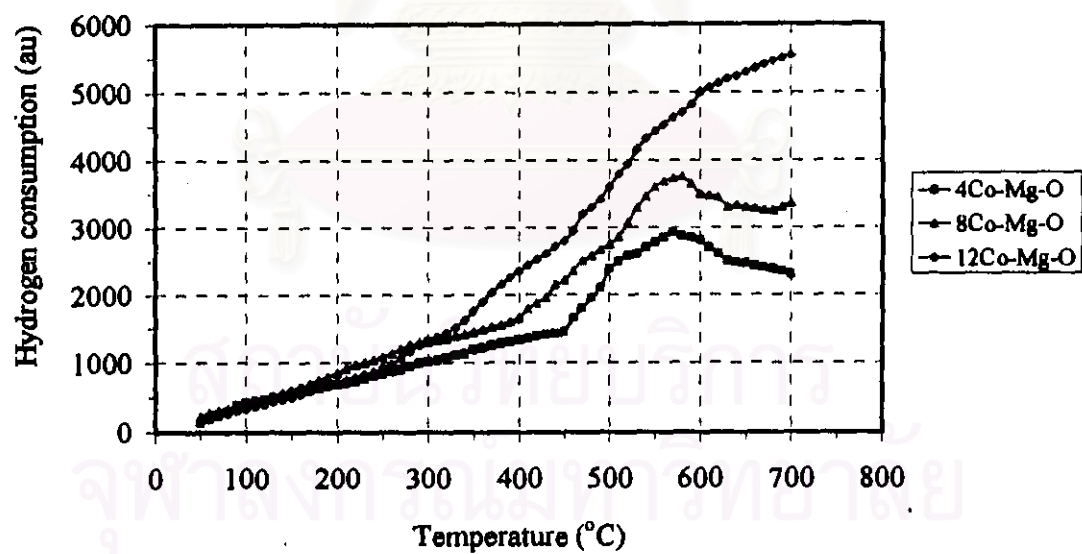


Figure 5.12 The TPR profile of Co-Mg-O catalysts.

5.1.4 Electron Spin Resonance (ESR)

In order to gain insight on the behavior of Co-Mg-O catalysts with varying cobalt concentration. The Electron Spin Resonance (ESR) spectrometer is used to detect Co-Mg-O species in catalyst which have unpaired electron therefore Co-Mg-O species which has no unpaired electron is not be detected by this method.

The characterization by ESR spectroscopy uses a “*g*” factor and unpaired electron number for comparing electronic structure of each catalyst. The *g* factor is a constant value specify for a system or material which are measured, *i.e.* it has different values when different materials are detected. The unpaired electron number are measured by area under the curve of ESR spectra.

The results of these experiments are shown in figures 5.13 - 5.15. Figure 5.13 shows ESR spectrum of fresh 4Co-Mg-O. The *g* value is 5.6910 and its unpaired electron number is 6.03×10^7 . ESR spectrum of fresh 8Co-Mg-O catalyst is presented in figure 5.14. A signal was observed that *g* value is remain at 5.6910 and unpaired electron number is 5.99×10^7 which is lower value than 4Co-Mg-O catalyst. Figure 5.15 demonstrates the ESR spectrum of fresh 12Co-Mg-O catalyst. The *g* value is 5.6910 which is the same value as 4Co-Mg-O and 8Co-Mg-O catalysts. While the unpaired electron number is 4.27×10^7 which is lower than the values of 4Co-Mg-O and 8Co-Mg-O catalysts.

The comparison of figures 5.13, 5.14, and 5.15 for the three catalysts give the same value at 5.6910. It suggests that Co-Mg-O should have the same structure of unpaired electron species in the catalyst. However when cobalt concentration in the catalyst increase, the decreasing amounts unpaired electron number. In other words, the amounts of Co-Mg-O species in Co-Mg-O catalyst which has no unpaired electron increase with increasing cobalt content.

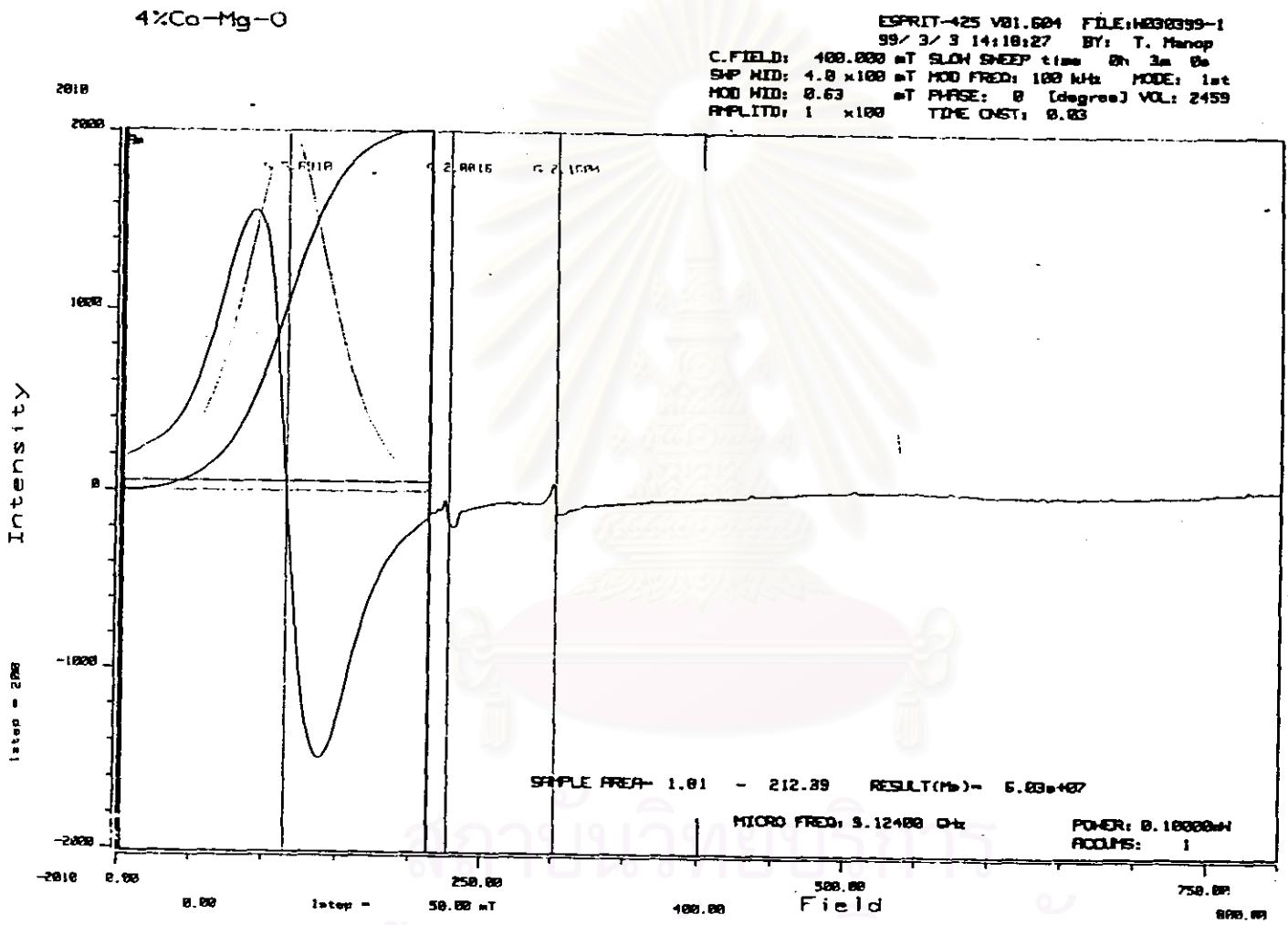


Figure 5.13 The ESR spectrum of 4Co-Mg-O catalyst.

8%Co-Mg-O

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C.FIELD: 400.000 mT SLOW SWEEP time 0h 3m 0s

SWP WID: 4.0 x100 mT MOD FREQ: 100 kHz MODE: 1st

MOD WID: 0.63 mT PHASE: 0 (degree) VOL: 2450

AMPLTD: 1 x100 TIME ONT: 0.63

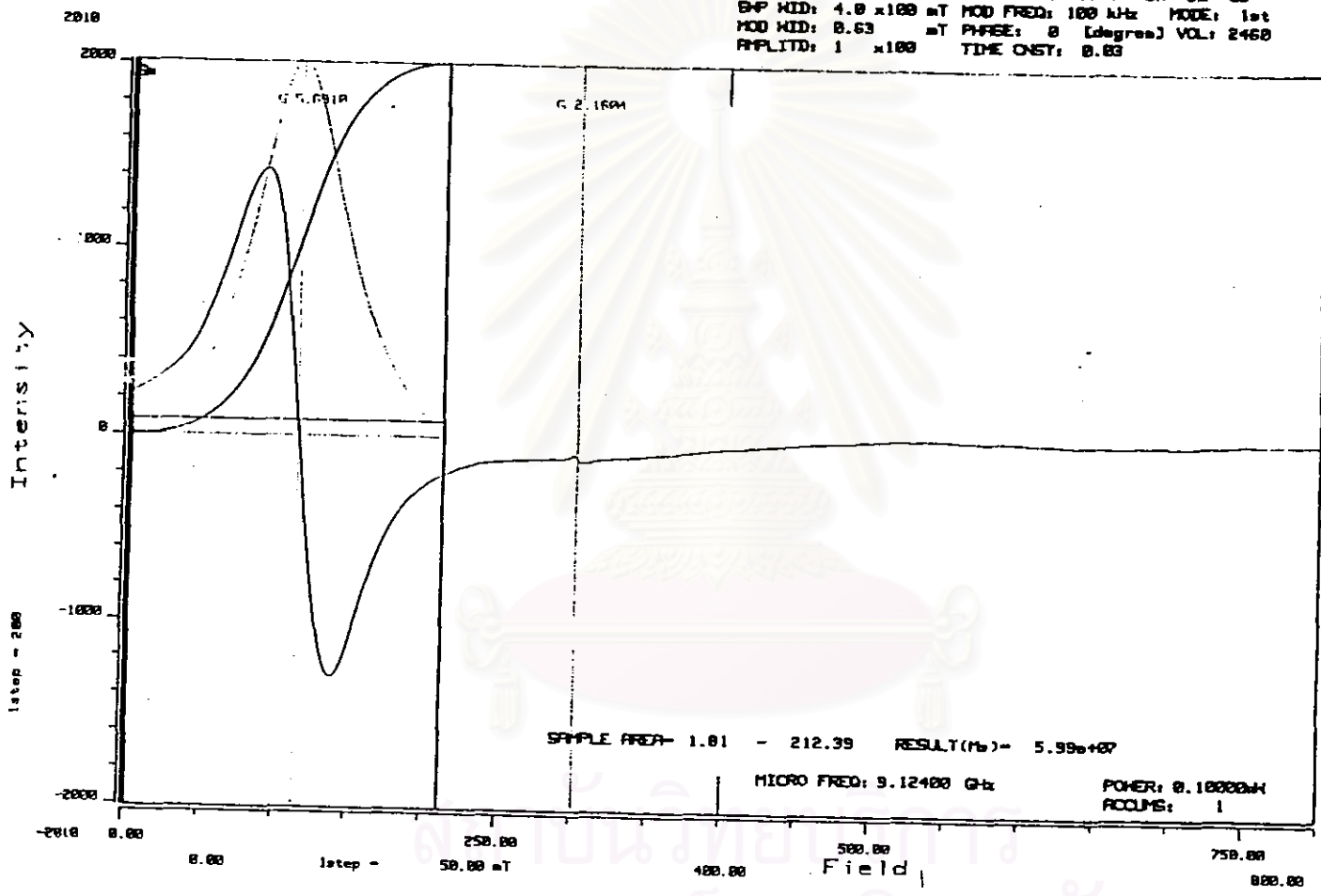


Figure 5.14 The ESR spectrum of 8Co-Mg-O catalyst.

12Co-Mg-O

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C.FIELD: 400.000 mT SLOW SNEEP time 0h 3m 0s

SWP WID: 4.0 x100 mT MOD FREQ: 100 kHz MODE: 1st

MOD WID: 0.63 mT PHASE: 0 [degree] VOL: 2450

AMPLTD: 1 x100 TIME ONST: 0.63

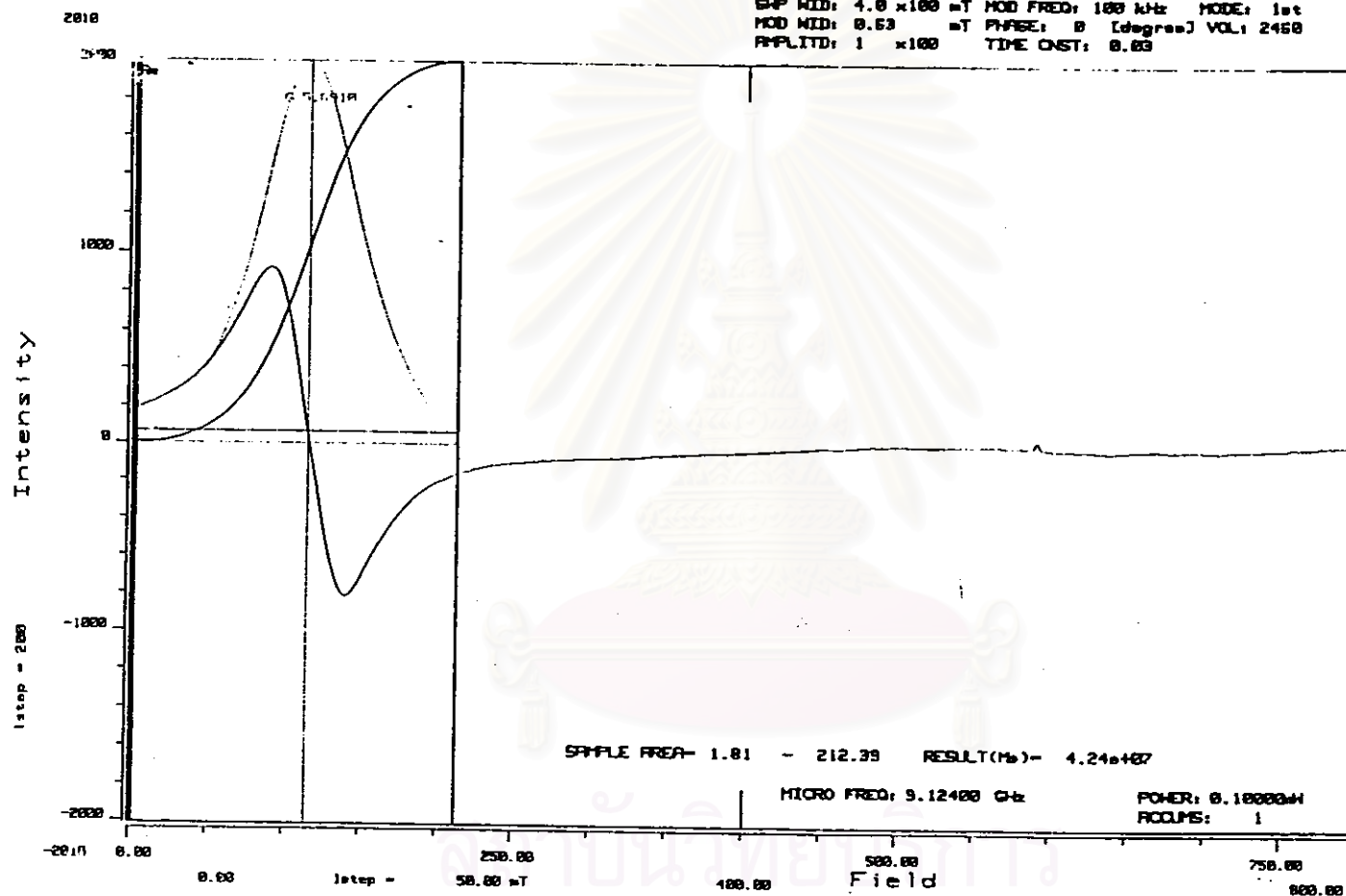


Figure 5.15 The ESR spectrum of 12Co-Mg-O catalyst.

5.2 Oxidation reaction

In this section, the oxidation property of Co-Mg-O catalysts having different cobalt concentration are performed by using the oxidation reaction on propane, 1-propanol, propene, and CO as test reaction.

5.2.1 Propane oxidation

- 4Co-Mg-O catalyst

The behavior of 4Co-Mg-O as a catalyst for propane oxidation in C_3H_8 : O_2 : N_2 mixtures is described in figure 5.16. Below 400°C the activity of this catalyst is not noticeable. When the reaction temperature is higher than 400°C the activity of catalyst occurs. The conversion of propane slightly increases from 0% to 5% when reaction temperature increases from 400°C to 500°C. All the reaction temperature the main reaction product observed is CO_2 with traces of propene.

- 8Co-Mg-O catalyst

Figure 5.17 shows the activity of 8Co-Mg-O catalyst for propane oxidation reaction. 8Co-Mg-O catalyst is more active than 4Co-Mg-O catalyst. At low reaction temperature the conversion of propane steadily increases from 1% to 8% with increasing reaction temperature from 350°C to 400°C. In the temperature range 400–425°C the activity of catalyst rapidly rises from 8% to 50%. Beyond 425°C, the conversion of propane gradually increases up to 68% at 500°C. At low propane conversion (350-400°C) the main reaction product is only CO_2 while at high propane conversion (400-500°C) the reaction product is CO_2 and there are some formation of other reaction products *ie*, methane, ethene, and propene. Consequently, the selectivity of CO_2 moderately falls from 100% to 55% and the selectivities of methane, ethene, and propene slightly rise from 3% to 5%, 30% to 34%, and 8% to 11%, respectively with increasing reaction temperature from 400°C to 500°C.

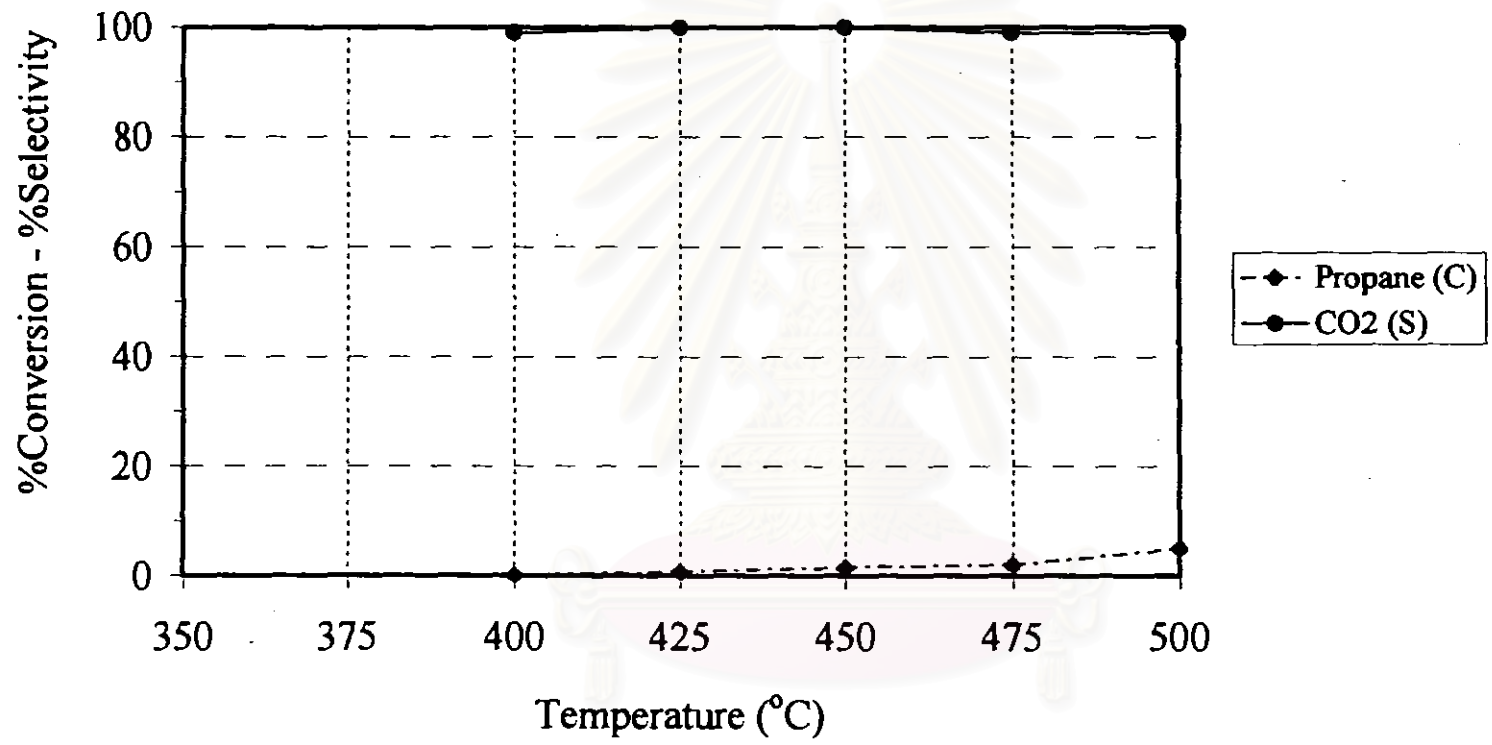


Figure 5.16 Conversion (C) of propane and product selectivities (S) on 4Co-Mg-O catalyst in the propane oxidation.

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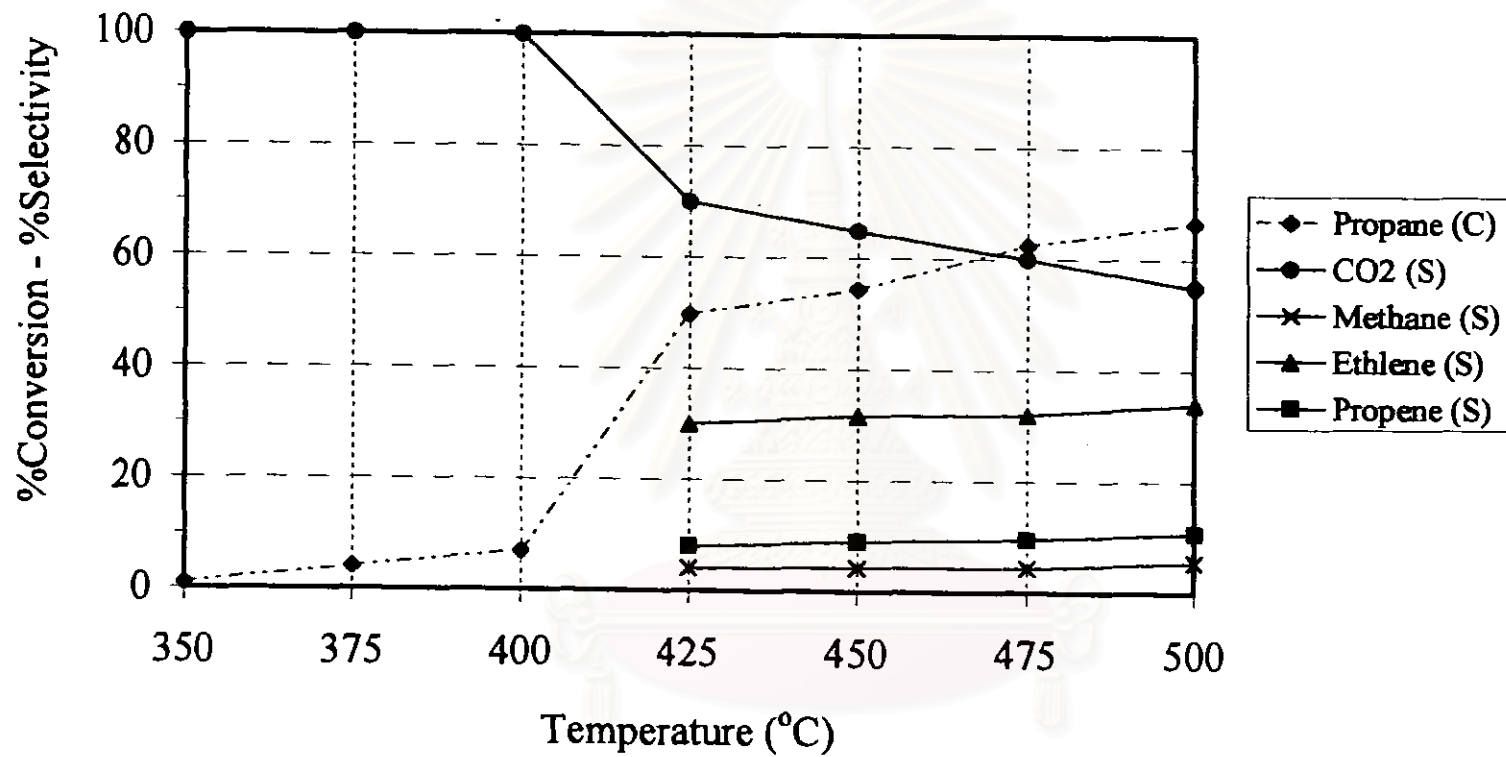


Figure 5.17 Conversion (C) of propane and product selectivities (S) on 8Co-Mg-O catalyst in the propane oxidation.

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From this results, the maximum selectivity of olefin (ethene and propene) of 8Co-Mg-O catalyst is about 45% and the maximum olefin yield is ca. 30% at 500°C.

- 12Co-Mg-O catalyst

The result of the catalytic oxidation of propane on 12Co-Mg-O catalyst is shown in figure 5.18. The oxidation of propane on 12Co-Mg-O catalyst is faster than that of 8Co-Mg-O and 4Co-Mg-O catalysts. The conversion of propane becomes detectable near 350°C. At low reaction temperature the activity of 12Co-Mg-O catalyst steadily increases from 2% to 6% propane conversion on the increase of temperature from 350°C to 375°C. The conversion of propane significantly rises up from 6% to 80% in the temperature range 375-425°C. Above 425°C, the propane conversion slightly increases and level off at 92% at 500°C.

At low propane conversion (350-400°C) the main reaction product is only CO₂ whereas at high propane conversion CO₂ is still dominant but there are some formation of other by products *i.e.* methane, ethene, and propene. At high propane conversion (above 400°C) the selectivity of CO₂ steadily goes down and levels off at about 85%. Nevertheless, the selectivities of methane, ethene, and propene remain constant at 1%, 8%, and 2%, respectively in the temperature range 425-500°C. The 12Co-Mg-O catalyst gives the maximum olefin selectivity is about 10% and the maximum olefin yield is ca. 10% at 500°C.

From propane oxidation reaction, it turns out that the activity of 8Co-Mg-O catalyst provides the highest olefin formation under the oxidation condition, the maximum olefin selectivity (45%) and the maximum olefin yield (30%) at 500°C.

The blank experiment was test for propane oxidation and found that no reaction takes place and MgO has no activity for the propane oxidation.

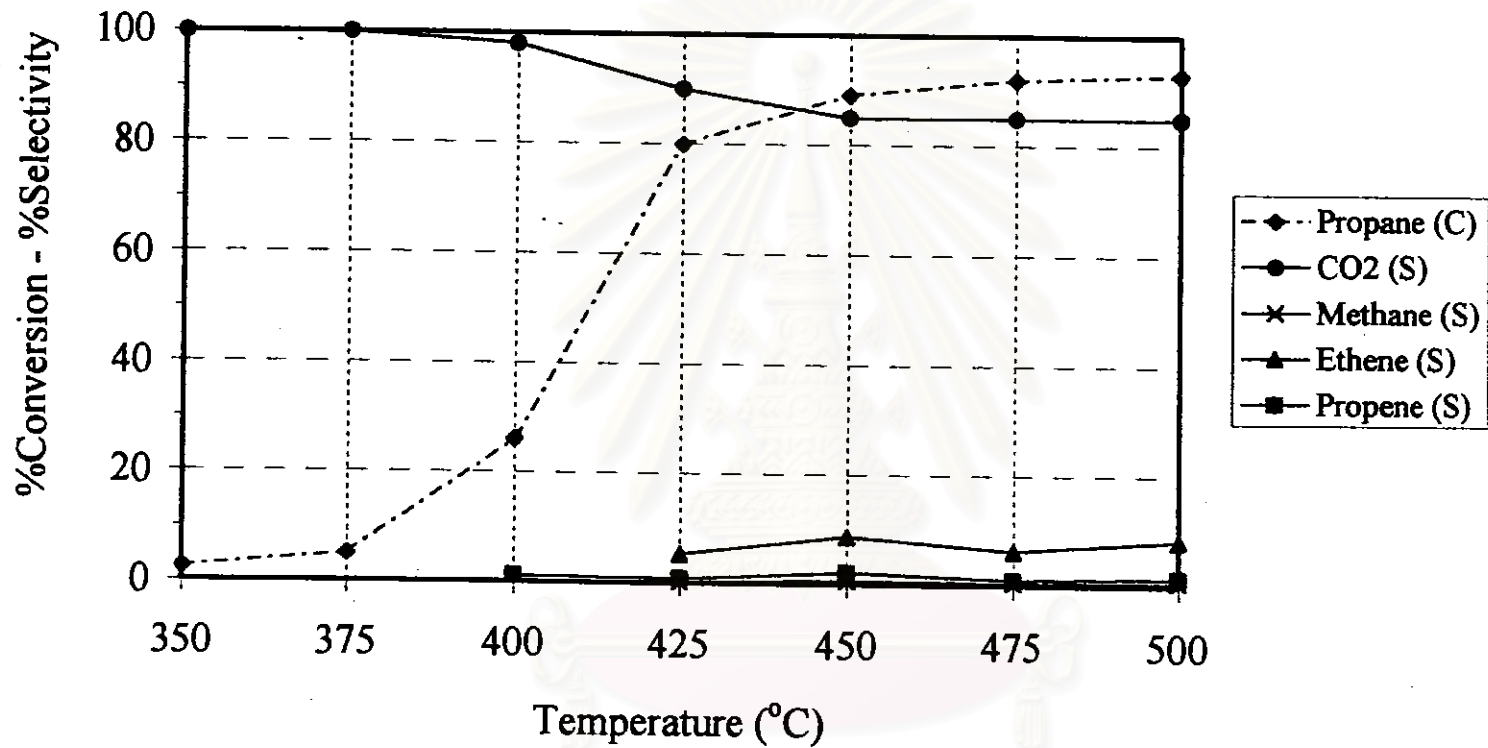


Figure 5.18 Conversion (C) of propane and product selectivities (S) on 12Co-Mg-O catalyst in the propane oxidation

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5.2.2 1- Propanol oxidation

- *MgO catalyst*

The catalytic property of MgO as catalyst for 1-propanol oxidation is demonstrated in figure 5.19. The oxidation of 1-propanol on MgO catalyst becomes observable at 100°C, while 1-propanol conversion approaches near 100% at 500°C. In the initial reaction temperature, the conversion of 1-propanol gradually increases from 1% to 10% on the increase of reaction temperature from 100°C to 250°C. When the reaction temperature is higher than 250°C the activity of this catalyst rapidly goes up to 100% at 500°C. At low 1-propanol conversion the main oxidation product is propanal with a small amount of CO₂. Instead at high 1-propanol conversion (above 250°C) propanal selectivity rapidly decreases while there are the formations of a large amount of CO₂ and small amounts of formaldehyde, ethene, and propene.

The maximum selectivity to CO₂ is ca. 93% at 500°C, ethene is ca. 20% at 450°C, propene is ca. 18% at 400°C, and formaldehyde is ca. 8% at 350°C. At 500°C, complete 1-propanol conversion occurs and selectivities to all products, except CO₂, fall to zero.

- *4Co-Mg-O catalyst*

Figure 5.20 demonstrates the behavior of 4Co-Mg-O catalyst. The 1-propanol oxidation on 4Co-Mg-O catalyst is faster than that of MgO catalyst (compare with figure 5.19). The conversion of 1-propanol on 4Co-Mg-O catalyst becomes observable at near 100°C. Beyond 150°C, the activity of this catalyst significant goes up to 100% at 500°C.

At low 1-propanol oxidation (100-150°C) the main reaction product is only propanal, whose selectivity decreases faster than MgO catalyst. On the other hand, at high 1-propanol oxidation the selectivity of propanal rapidly declines to zero at near 350°C and the formation of CO₂, ethene, and formaldehyde occurs. Selectivity of

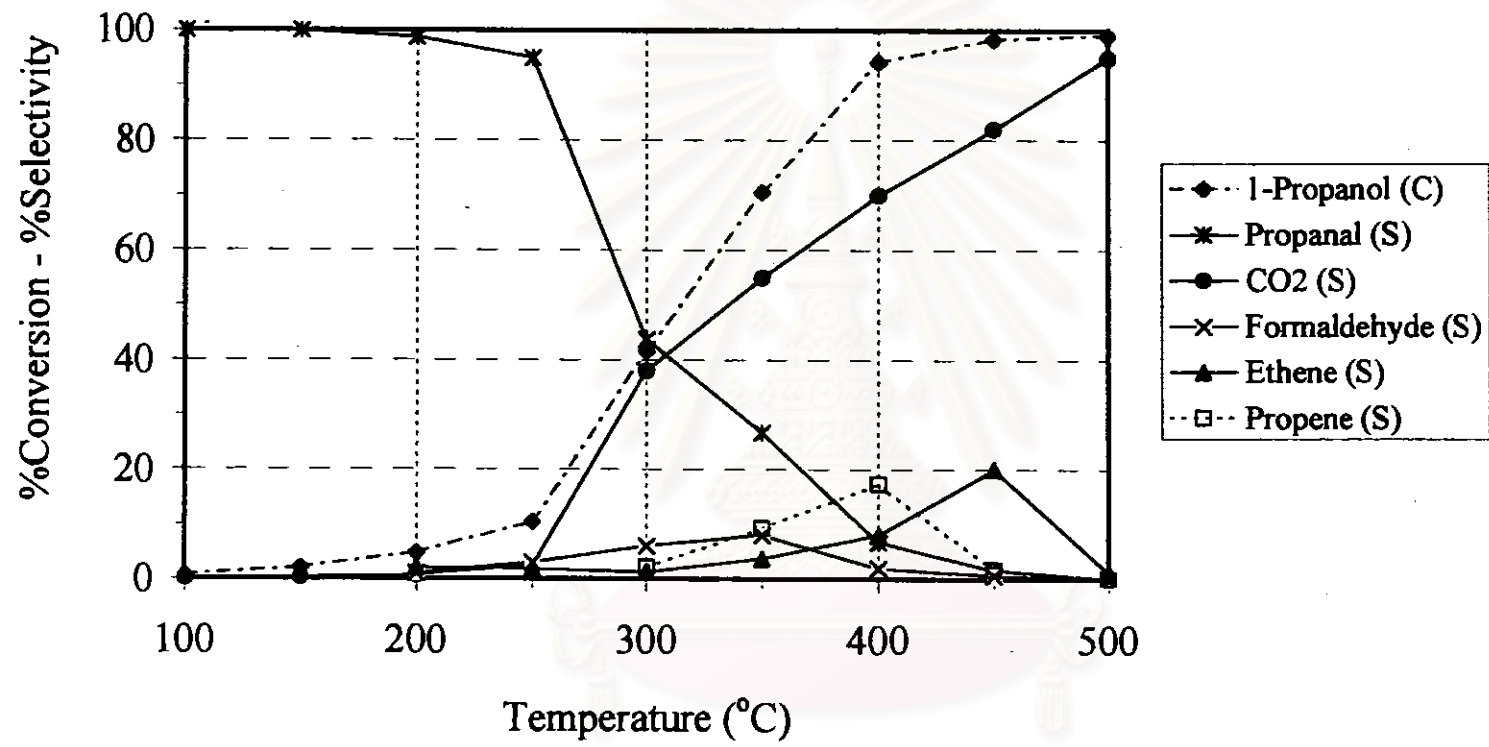


Figure 5.19 Conversion (C) of 1-propanol and product selectivities (S) on MgO catalyst in the 1-propanol oxidation.

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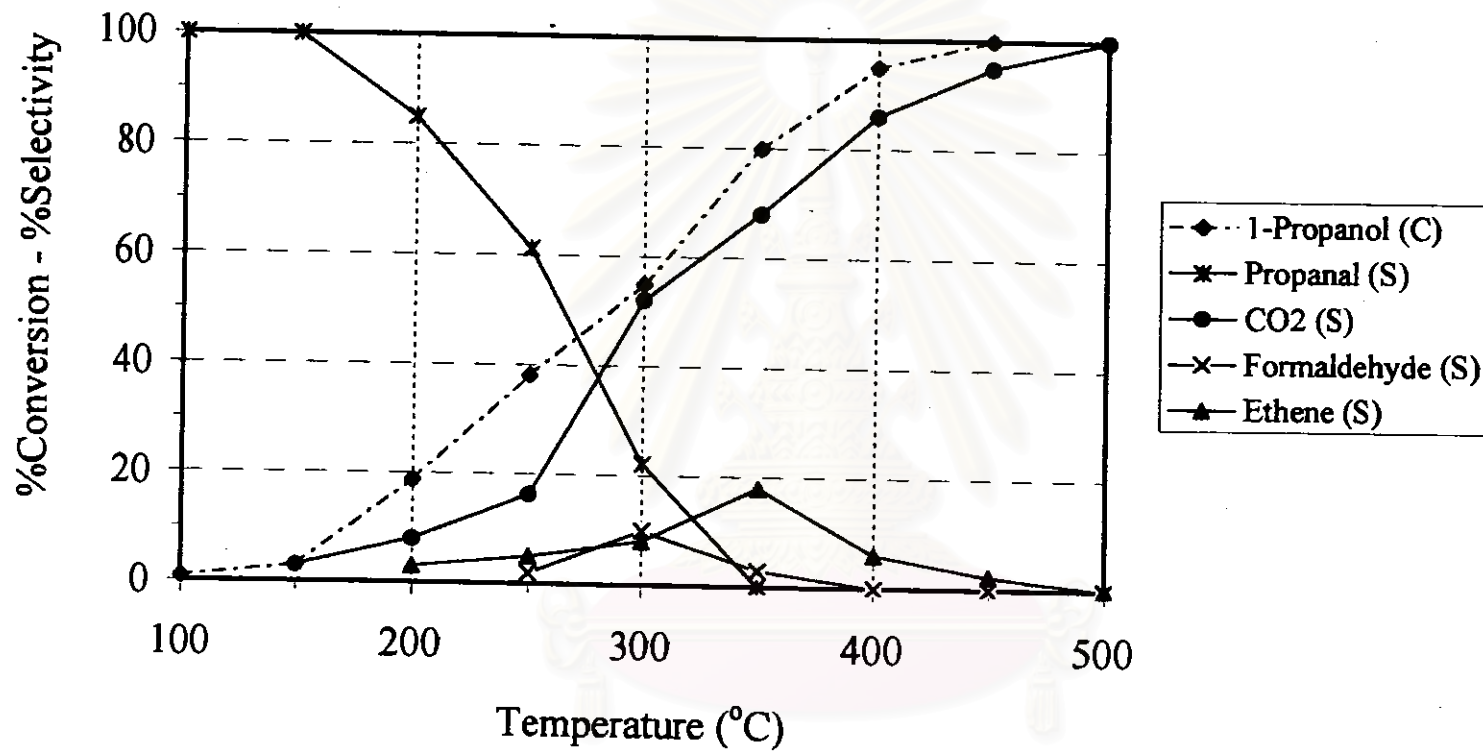


Figure 5.20 Conversion (C) of 1-propanol and product selectivities (S) on 4Co-Mg-O catalyst in the 1-propanol oxidation.

CO₂ significantly rises and reaches 100% at around 450°C while the maximum selectivities of formaldehyde and ethene are detected at different reaction temperature. No propene is observed among the reaction products at all reaction temperature.

The maximum selectivity to CO₂ is 100% at 500°C, ethene is 18% at 350°C, and formaldehyde is 10% at 300°C. At reaction temperature higher than 450°C, 1-propanol conversion becomes total and selectivities to all partial oxidation products drop to zero.

- 8Co-Mg-O catalyst

The behavior of 8Co-Mg-O catalyst for the 1-propanol oxidation is described in figure 5.21. The pattern of 1-propanol conversion and the type of reaction products of 8Co-Mg-O catalyst are similar to 4Co-Mg-O and MgO catalysts. However, the activity of 8Co-Mg-O catalyst is stronger than that 4Co-Mg-O and MgO catalysts. 1-Propanol conversion is detectable at only 100°C, while 1-propanol conversion become total at temperature higher than 400°C. At low 1-propanol conversion, propanal selectivity is 100%, while on the increase of reaction temperature causes selectivity to propanal suddenly falls to zero faster than 4Co-Mg-O and MgO catalysts and there are the formation of CO₂, formaldehyde, and ethene.

A broad selectivities in ethene and formaldehyde are observed at the temperature range 150-350°C. The maximum selectivity of CO₂ is 100 % at 450°C, ethene is 2% at 200°C, and formaldehyde is ca. 13% at 250°C.

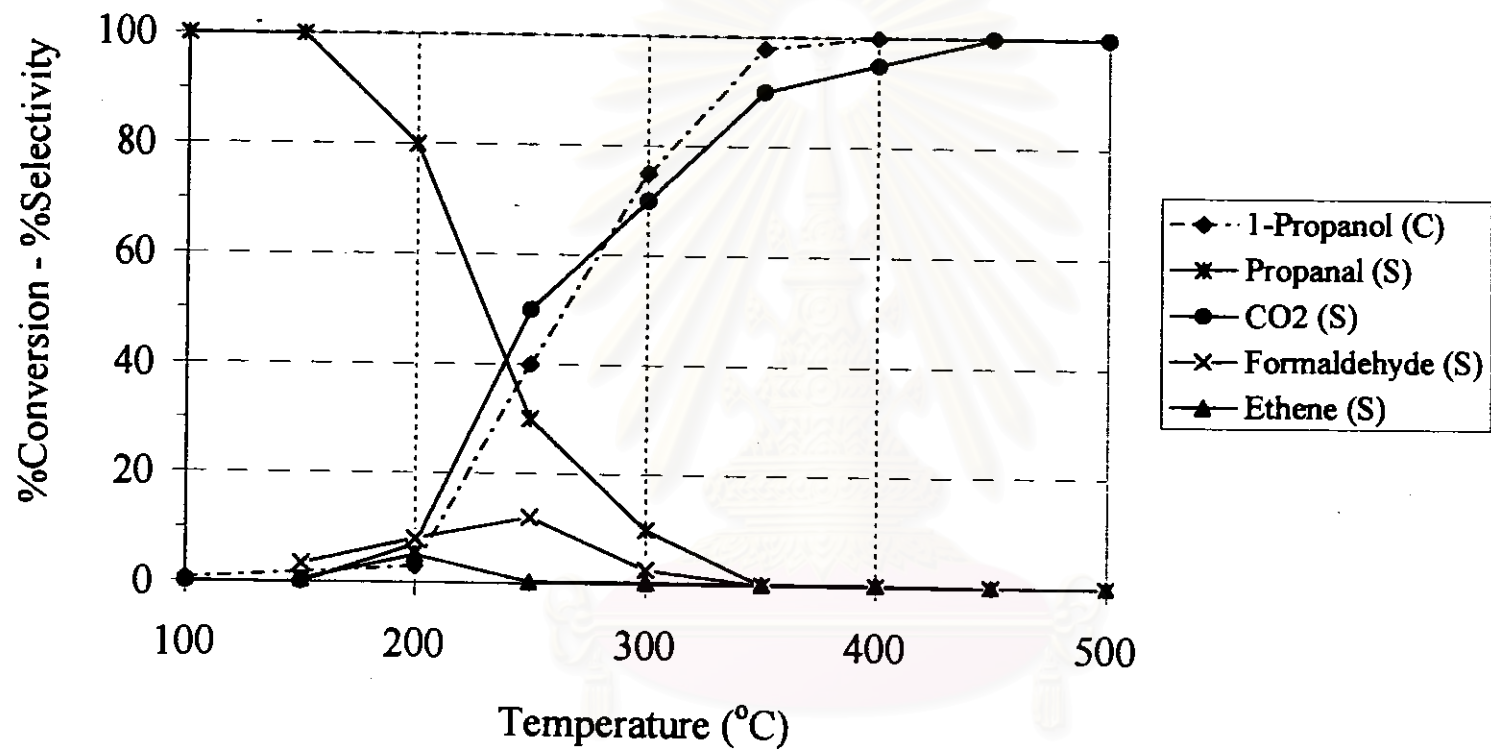


Figure 5.21 Conversion (C) of 1-propanol and product selectivities (S) on 8Co-Mg-O catalyst in the 1-propanol oxidation.

-12Co-Mg-O catalyst

The catalytic activity of 12Co-Mg-O as catalyst for 1-propanol oxidation is presented in figure 5.22. The behavior of 12Co-Mg-O catalyst is similar to MgO, 4Co-Mg-O, and 8Co-Mg-O catalysts. However, the oxidation of 1-propanol on 12Co-Mg-O catalyst is faster than that of 8Co-Mg-O, 4Co-Mg-O, and MgO catalysts, respectively. The 1-propanol oxidation becomes significant at reaction temperature higher than 100°C and attains near totality when reaction temperature is approaching 350°C. At low 1-propanol conversion, the selectivity of propanal is 100%. While at high 1-propanol conversion propanal production rapidly falls to zero faster than 8Co-Mg-O, 4Co-Mg-O and MgO catalysts whereas the formation of CO₂ is large and formaldehyde is small with some traces of ethene. The CO₂ selectivity becomes 100% at the reaction temperature higher than 350°C. The maximum selectivity of formaldehyde is about 22% at 200°C. After 400°C, 1-propanol conversion becomes total and selectivity to CO₂ is 100%, while formaldehyde selectivity gradually drops to zero.

Figures 5.23-5.28 summarize the effect of cobalt loading on the 1-propanol conversion and selectivity of product in the 1-propanol oxidation reaction.

Figure 5.23 shows the conversion of 1-propanol against reaction temperature. From this figure, MgO and Co-Mg-O catalysts show the similar catalytic activity for 1-propanol oxidation. However, when amount of loading cobalt is increased, the conversion of Co-Mg-O catalyst increases. It means that cobalt increases the catalytic activity of Co-Mg-O catalyst. From this result the 12Co-Mg-O catalyst shows the highest activity for 1-propanol conversion. The catalytic activity of these catalysts are in the order: 12Co-Mg-O > 8Co-Mg-O > 4Co-Mg-O > MgO.

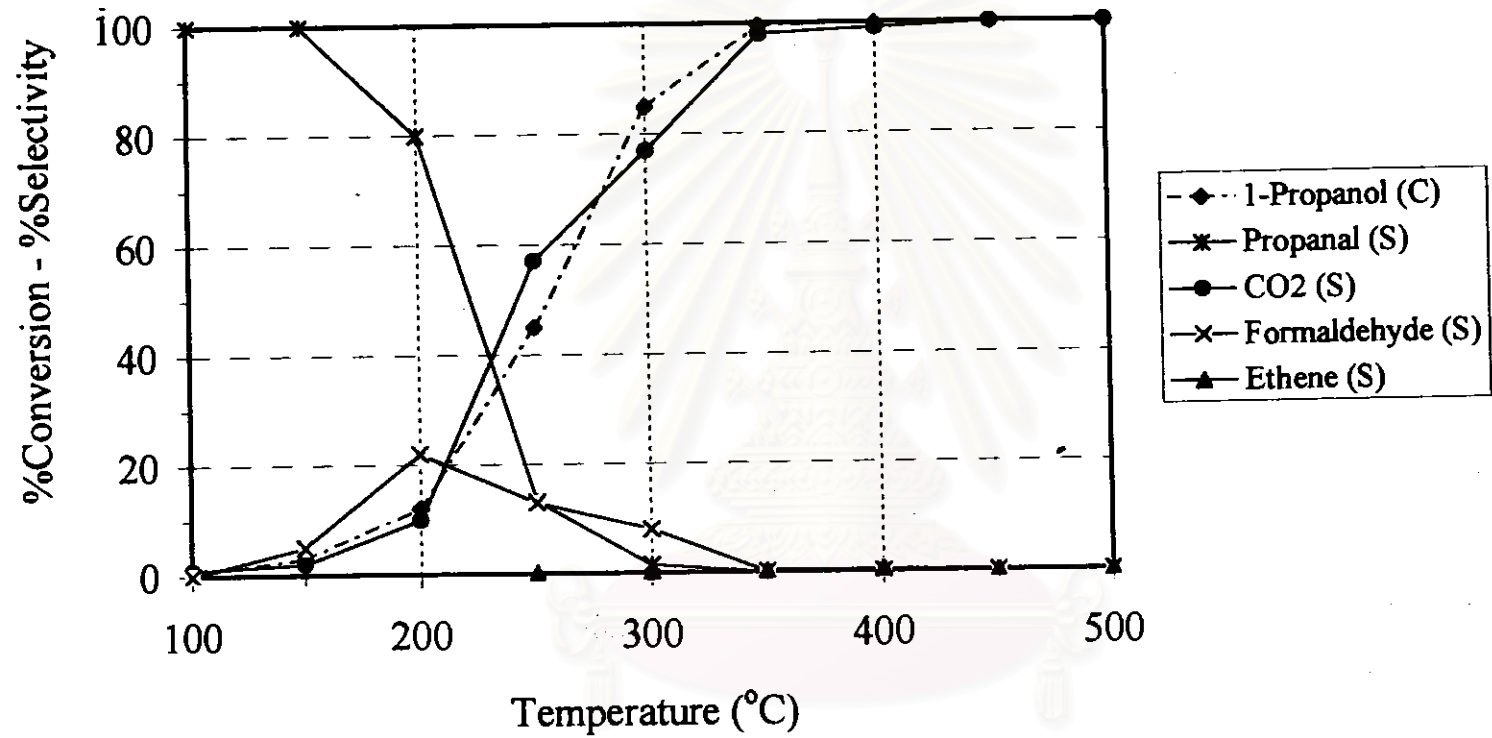


Figure 5.22 Conversion (C) of 1-propanol and product selectivities (S) on 12CoMgO catalyst in the oxidation of 1-propanol.

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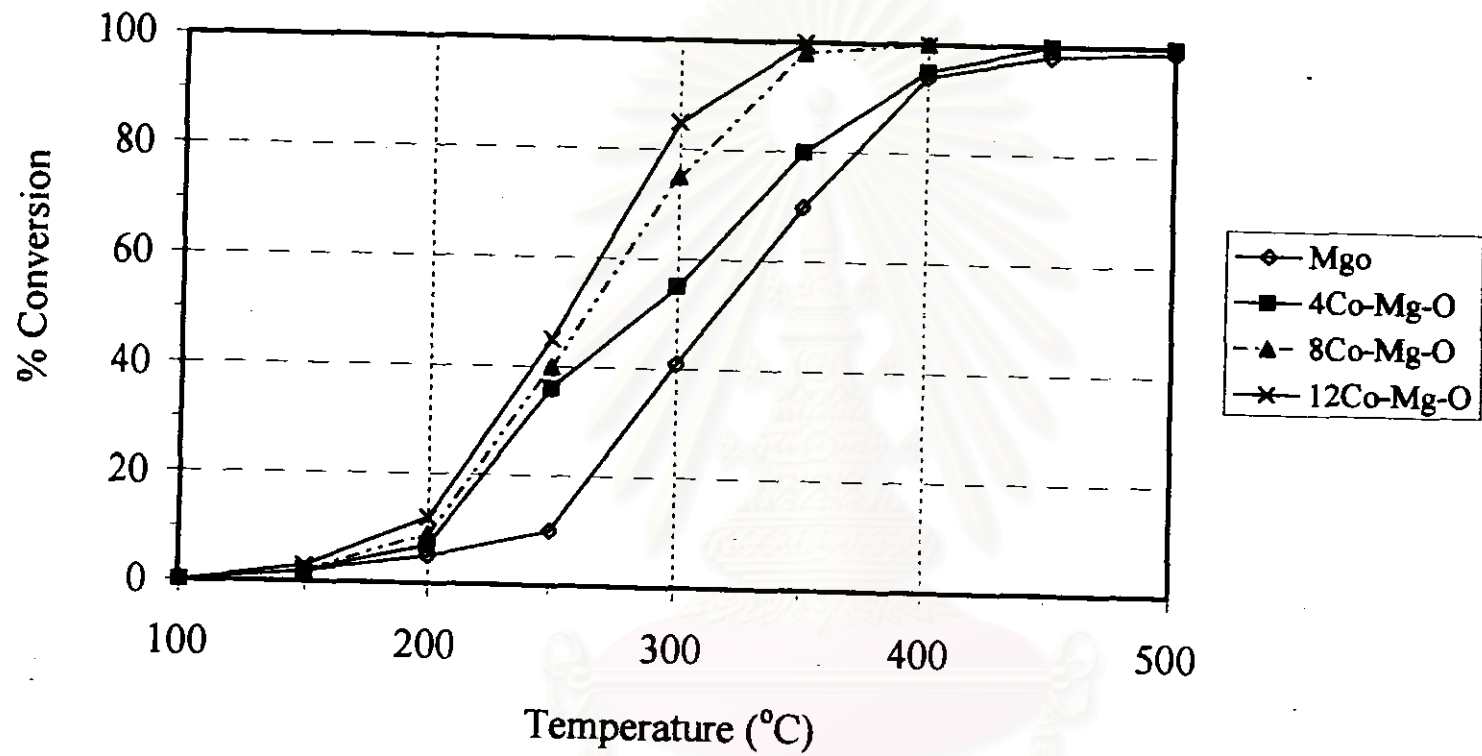


Figure 5.23 1- Propanol conversion on Co-Mg-O and MgO catalysts in the 1-propanol oxidation.

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The effect of cobalt concentration on propanal selectivity is more clearly demonstrated in figure 5.24 where the selectivities are plotted against the reaction temperature over MgO, 4Co-Mg-O, 8Co-Mg-O, and 12Co-Mg-O catalysts. These catalysts give the similar patterns for propanal selectivities. At low reaction temperature the selectivities of Co-Mg-O and MgO catalysts are near 100%. However, at high reaction temperature the propanal selectivity of all the catalysts rapidly go down to zero with increasing reaction temperature. The MgO catalyst can sustain higher propanal selectivity than 4Co-Mg-O, 8Co-Mg-O, and 12Co-Mg-O catalysts, respectively. These data suggest that the formation of propanal prefer to occur on MgO catalyst than Co-Mg-O catalyst.

Figure 5.25 exhibits the selectivities of formaldehyde on Co-Mg-O catalysts against the reaction temperature. The formation of formaldehyde on Co-Mg-O catalysts is different depends on the amount of cobalt concentration in the catalyst. If the cobalt content in catalyst is high formaldehyde is easy to form at low reaction temperature with a high value of formaldehyde selectivity. On the other hand, when cobalt loading in catalyst is low, formaldehyde forms at higher oxidation temperature with lower formaldehyde selectivity. The 12Co-Mg-O catalyst gives the highest formaldehyde selectivity at 200°C in the 1-propanol oxidation. While MgO catalyst yields the lowest formaldehyde selectivity at 350°C. From this data, the formaldehyde selectivity can be affected by the cobalt concentration. The highest selectivity of formaldehyde for each catalyst decreases in the order: 12Co-Mg-O > 8Co-Mg-O > 4Co-Mg-O > MgO catalysts.

The behavior of ethene selectivity is exhibited in figure 5.26. Ethene prefers to form on MgO catalyst than Co-Mg-O catalyst. However, on the MgO catalyst the reaction temperature should be high and the level of ethene selectivity is high. When cobalt is incorporated in to the catalyst, the ethene is easy to form at lower reaction temperature but the value of ethene selectivity gradually declines. The highest ethene selectivity (20% at 450°C) is observed on MgO catalyst and the highest ethene selectivity in each catalyst for 1-propanol oxidation decreases in the order:

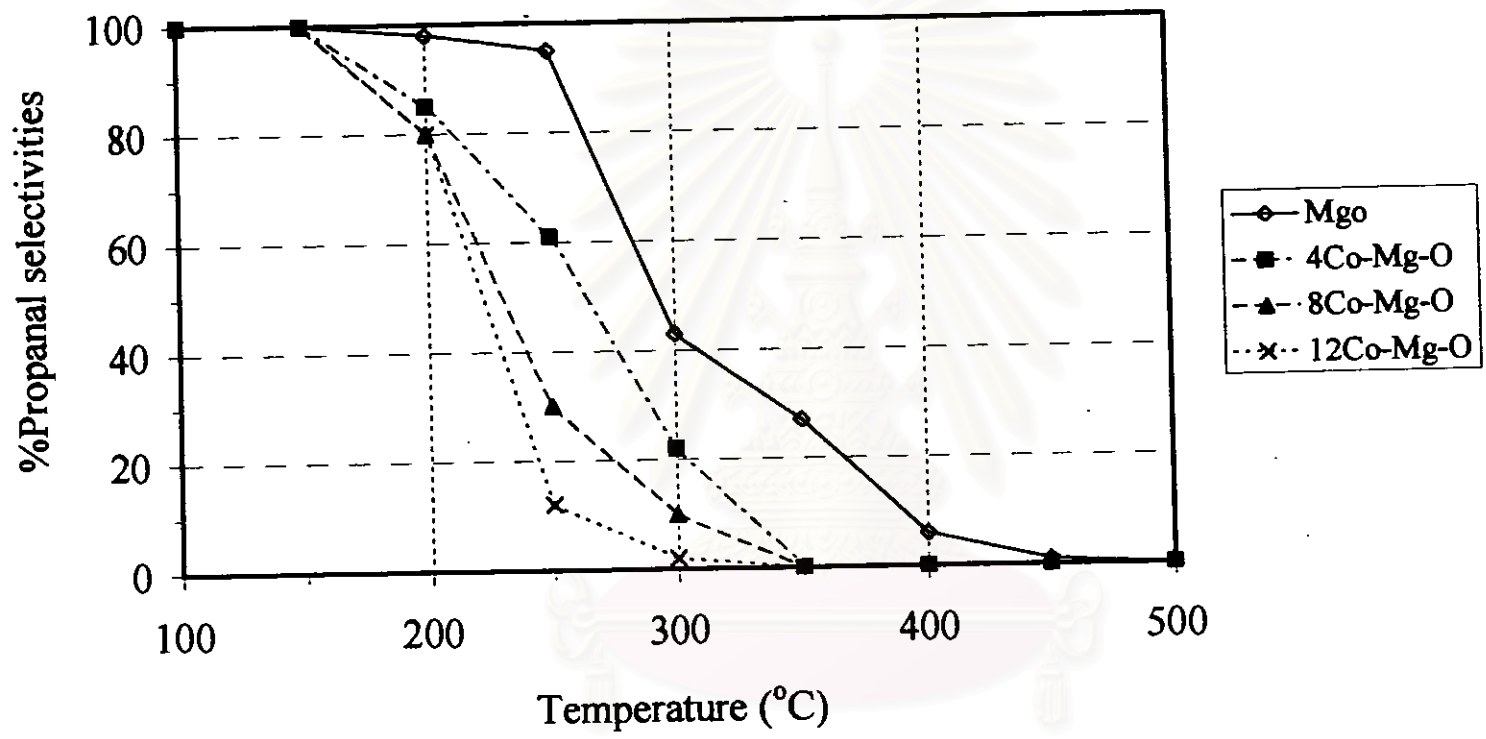


Figure 5.24 Propanal selectivities on Co-Mg-O and MgO catalysts in the 1-propanol oxidation.

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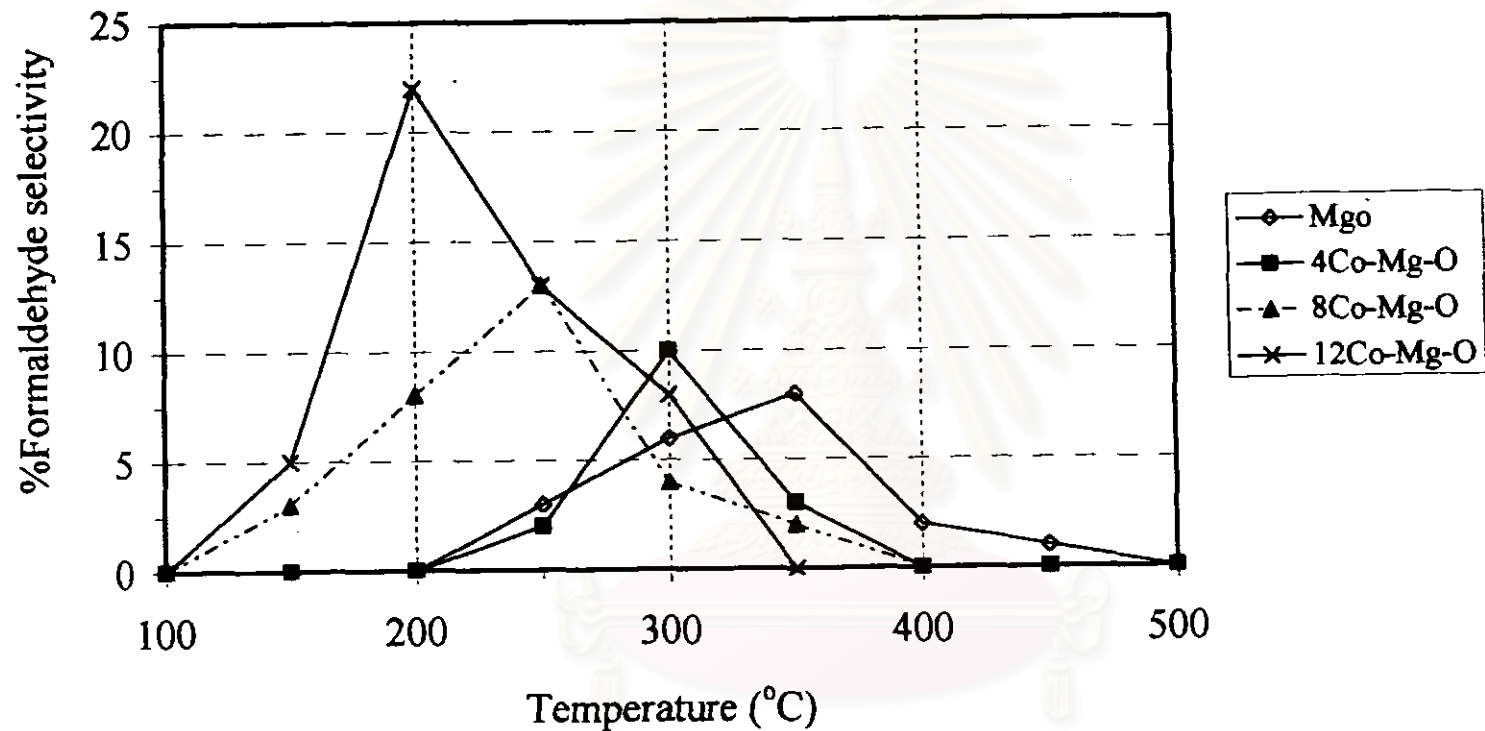


Figure 5.25 Formaldehyde selectivities on Co-Mg-O and MgO catalysts in the 1-propanol oxidation.

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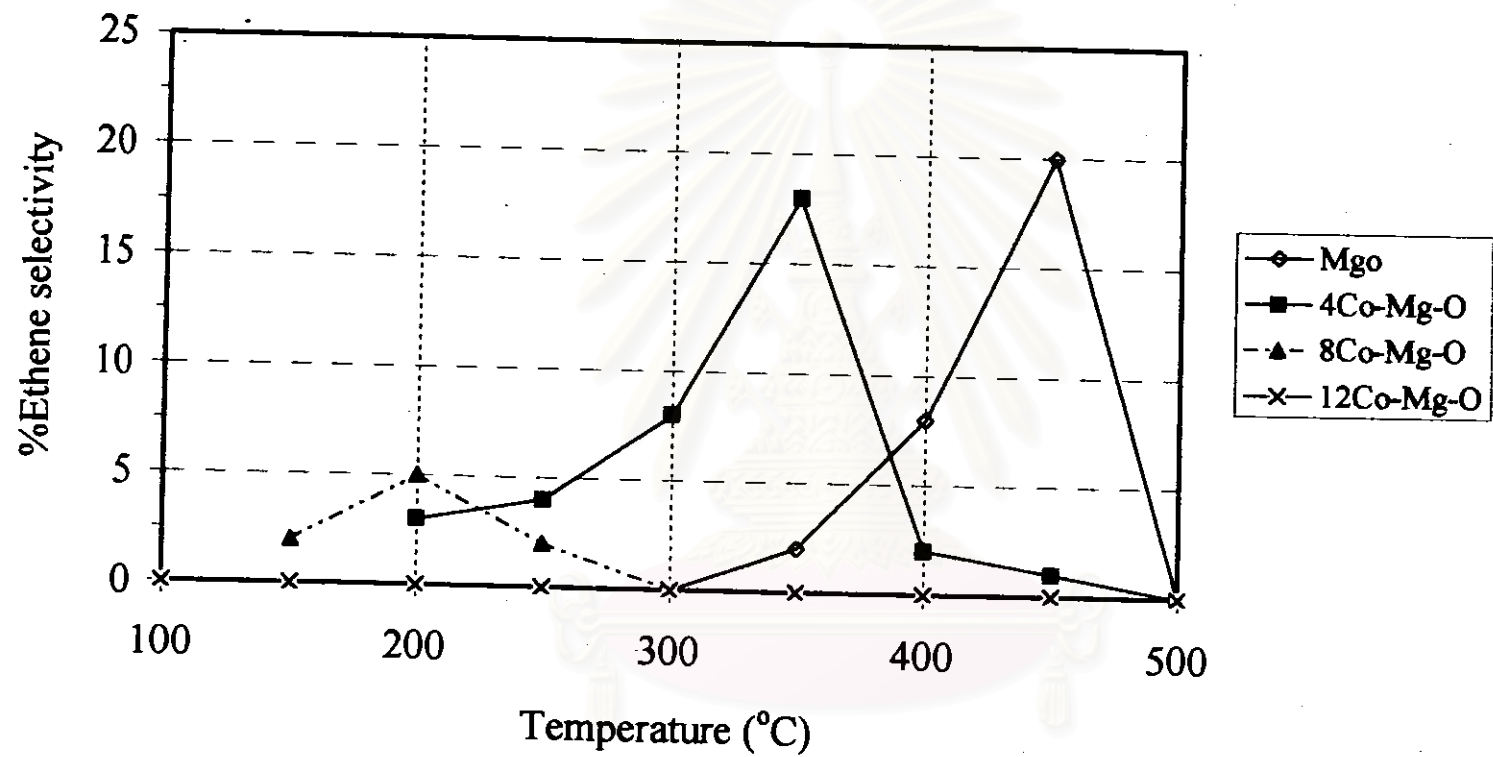


Figure 5.26 Ethene selectivities on Co-Mg-O and MgO catalysts in the 1-propanol oxidation.

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MgO, 20% > 4Co-Mg-O, 17% > 8Co-Mg-O, 5% > 12Co-Mg-O, 0% (for all reaction temperature).

Figure 5.27 shows the CO₂ selectivity versus the cobalt concentration. All catalysts (MgO and Co-Mg-O catalysts) give similar behavior of CO₂ selectivity for 1-propanol oxidation. In the reaction temperature range about 100°C-200°C the value of CO₂ selectivity is low. When the oxidation temperature is higher than 200°C, CO₂ selectivity rapidly increases and approaches about 100% at 500°C for all of these catalysts. However, 12Co-Mg-O catalyst gives the highest value of CO₂ selectivity while MgO catalyst provides the lowest level of CO₂ selectivity. The selectivity of CO₂ falls in the order: 12Co-Mg-O > 8Co-Mg-O > 4Co-Mg-O > MgO.

5.2.3 Propene oxidation

The oxidation of propene was performed on 4Co-Mg-O catalyst (figure 5.28) over the temperature range 100-500°C. The propene conversion starts at about 250-300°C. The propene conversion rapidly increases from 2% to 75% when temperature goes up from 300°C to 350°C. Beyond 350°C, the steady increase of propene conversion becomes total at 500°C. The main reaction product is only CO₂ at all temperature reaction. No CO and oxygenate is detected in this oxidation reaction.

5.2.4 CO oxidation

The CO oxidation was tested on 4Co-Mg-O catalyst in the temperature range 100-500°C. The result of this catalyst is shown in figure 5.29. The conversion of CO becomes detectable at about 100°C. At the temperature higher than 150°C the activity of this catalyst rapidly rises from 4% to 100% with increasing reaction temperature from 150°C to 300°C. The main reaction product is only CO₂ all the reaction temperature.

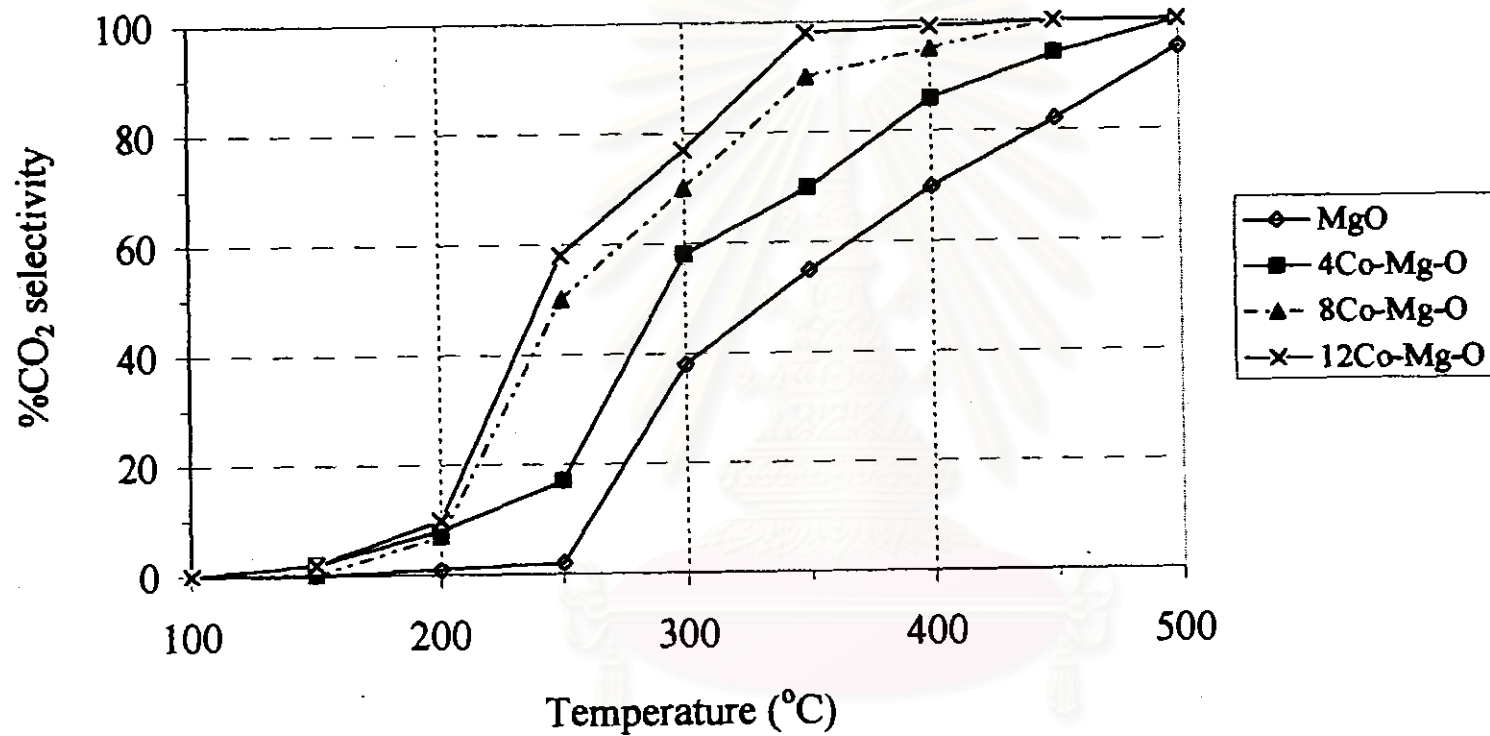


Figure 5.27 CO₂ selectivities on Co-Mg-O and MgO catalysts in the 1-propanol oxidation.

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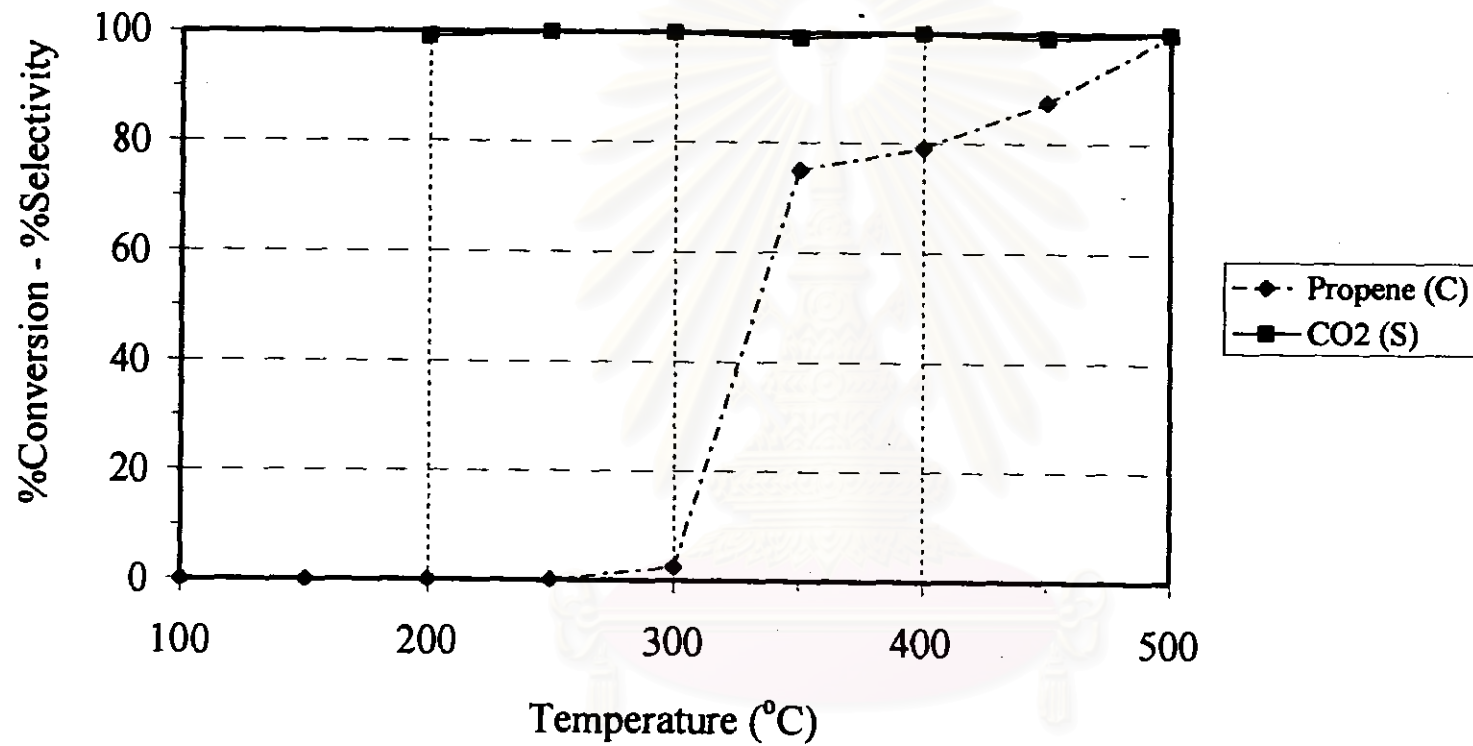


Figure 5.28 Conversion (C) and product selectivities (S) on 4Co-Mg-O catalyst in the oxidation of propene.

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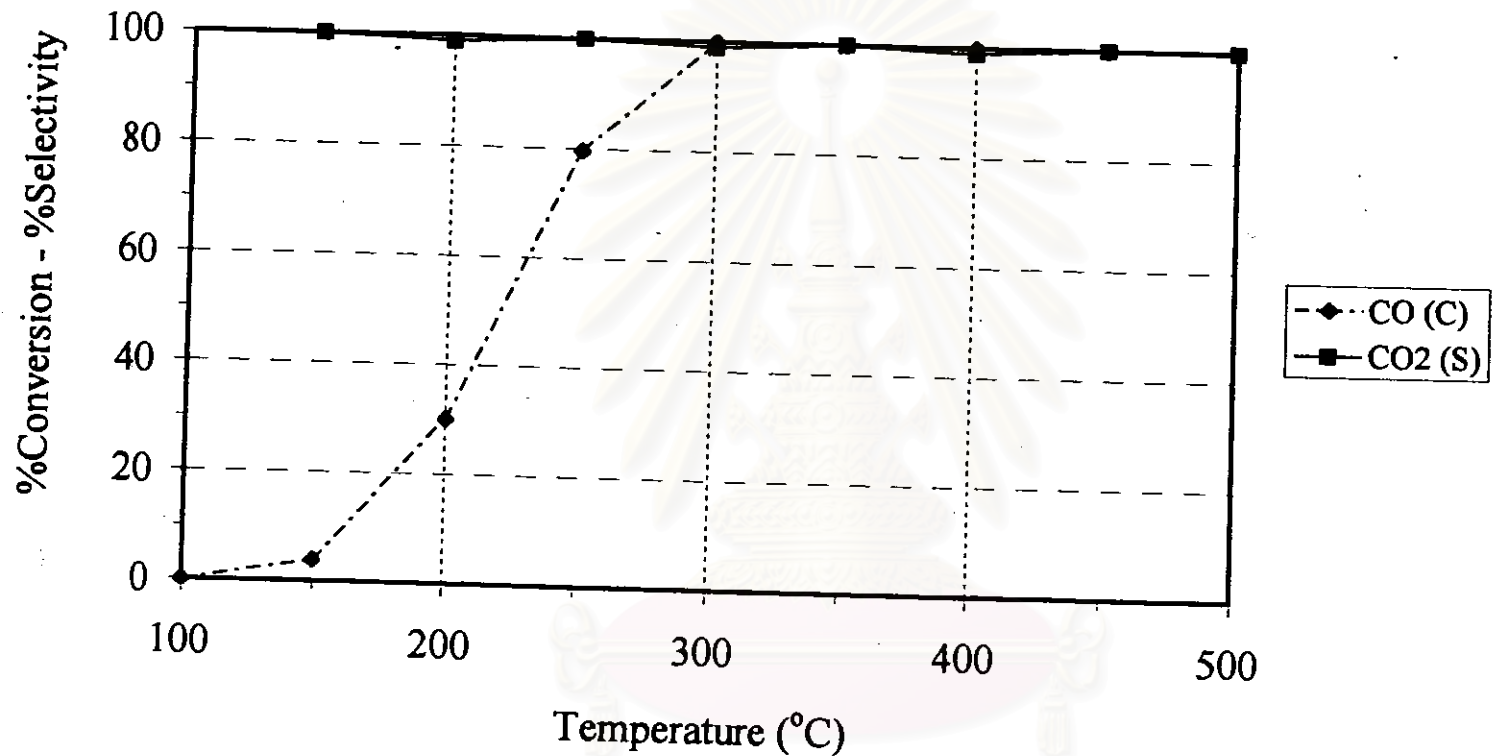


Figure 5.29 Conversion (C) and product selectivities (S) on Co-Mg-O catalyst in the CO oxidation.

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5.2.5 Catalytic property of Co-Mg-O catalyst

From the FTIR data, Co-Mg-O catalyst shows the same IR spectra as detect on MgO catalyst. These results suggest that in these regions, the IR spectra of cobalt oxide may be hidden by the adsorption band of MgO or there is no cobalt oxide forms in Co-Mg-O catalyst. As a result, FTIR can detect only spectra of MgO catalyst. When the catalyst was analyzed by XRD technique, the structure of Co-Mg-O catalyst is similar to that of MgO. This means that the structure of Co-Mg-O catalyst may form too small crystalline phase or thin layer so that the XRD technique can not detect.

To investigate the oxidation property of Co-Mg-O catalyst, several reactants *i.e.* propane, 1-propanol, propene, and CO are used to test catalytic activity. From the results of oxidation reactions, 8Co-Mg-O catalyst shows the highest catalytic performance for the oxidation of propane to olefin and the catalytic property of the catalyst strongly depends on the catalyst composition. 8Co-Mg-O catalyst gives the highest olefin selectivity (40%) and the highest olefin yield (30%) at 500°C. Therefore, 8Co-Mg-O catalyst is a suitable catalyst for propane oxidation under this reaction condition because this catalyst is active and selective for the oxidation of propane to olefin. In the case of 1-propanol oxidation reaction, at low 1-propanol conversion Co-Mg-O and MgO catalysts behave as selective catalysts. However, at high reaction temperature Co-Mg-O and MgO catalysts play role as combustion catalysts due to the fact that 1-propanol totally converts to CO₂ and H₂O. For propene and CO oxidation, 4Co-Mg-O catalyst plays role as a combustion catalyst.

From the consequence of oxidation of four reactants, Co-Mg-O catalyst is proper for propane oxidation because it is selective to form olefin from propane reactant. The behavior of Co-Mg-O catalyst with varying cobalt concentration on propane oxidation is elucidated by using TPR technique.

From previous TPR data of 4Co-Mg-O catalyst, the oxide on the surface of Co-Mg-O catalyst is reduced at the temperature higher than 450°C. This is the reason

why 4Co-Mg-O catalyst becomes active for propane oxidation at the temperature higher than 450°C. The reaction products is detected only CO₂ with a small amount of propene.

While 4Co-Mg-O catalyst has low activity for the propane oxidation, 8Co-Mg-O catalyst behaves in different way. 8Co-Mg-O catalyst is rather active and selective than 4Co-Mg-O catalyst. 8Co-Mg-O catalyst gives higher conversion of propane, ca. 70%, and provides high a selectivity of olefin 40% at 500°C. 8Co-Mg-O catalyst gives the advantage of olefin selectivity over other selective oxidation catalyst because the selectivity of olefin does not fall when the reaction temperature rises. On the other hand, for propane oxidation the olefin selectivity on other selective catalysts, such as V-Mg-O and MgMoO catalysts decreases with increasing reaction temperature [e.g. Chaar *et al.* (1988) and Yoon *et al.* (1995a)]. The TPR pattern of 8Co-Mg-O catalyst indicates that the oxide on the surface of 8Co-Mg-O catalyst is reduced in a large amount at the reduction higher than 400°C. For that reason, the conversion of propane on 8Co-Mg-O catalyst is significantly increased at the reaction temperature above 400°C.

Contrary to 8Co-Mg-O catalyst, 12Co-Mg-O catalyst is more active for propane oxidation than 8Co-Mg-O catalyst. However, it is less selective to form olefin than 8Co-Mg-O catalyst. The maximum olefin selectivity of 12Co-Mg-O catalyst is about 10% and the maximum olefin yield is ca. 10% at 500°C. The conversion of propane rapidly rises at the temperature higher than 375°C. TPR data of 12Co-Mg-O catalyst shows that a large amount of the oxide on the surface of catalyst is reduced at the reduction temperature beyond 375°C. However, the olefin selectivity for 12Co-Mg-O catalyst is lower than 8Co-Mg-O catalyst. The TPR profiles inform that, the oxides on 12Co-Mg-O catalyst is more reduced than 8Co-Mg-O catalyst. Accordingly, the olefin which forms from propane on 12Co-Mg-O catalyst will be further oxidized to CO₂. Thus the olefin selectivity declines.

For propane oxidation reaction on 8Co-Mg-O and 12Co-Mg-O catalysts, at low reaction temperature there is only the formation of CO₂ while at high reaction

temperature there are the formation of CO_2 and other reaction products *i.e.* methane, ethene, and propene. These results suggest that the activation energy (E_a) of CO_2 may be lower than methane, ethene, and propene so that low reaction temperature is enough for the formation of CO_2 . At high reaction temperature the reactant has high enough energy for the formation of methane, ethene, and propene. Consequently, we can observe CO_2 at all reaction temperature and detect methane, ethene, and propene at high reaction temperature.

However, for 4Co-Mg-O catalyst only CO_2 is detected as reaction product. Because 4Co-Mg-O catalyst is very low active for the propane oxidation. Very small amount of methane, ethene, and propene may be form together with CO_2 . Accordingly, there is only CO_2 is measurable as reaction product at all reaction temperature.



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