CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are divided into two major parts including the catalyst characterization and the catalytic test by the oxidation of propane, propene, 1-propanol and carbon monoxide.

5.1 Catalyst Characterization

5.1.1 Determination of composition content of catalyst and surface area

The compositions and the BET surface areas of all catalysts which are determined by AAS and BET surface area measurement are listed in Table 5.1.

Table 5.1 The compositions of catalysts and BET surface areas

Catalyst	%V[a]	%Mg[b]	Surface area (m^2/g)
5*VTi	4.82	-	7.34
5V1MgTi	4.65	1.28	8.37
co-5V1MgTi	4.99	1.25	8.28
1Mg 5VTi	4.82	1.20	8.30
5V2MgTi	4.65	1.89	8.14
3V2MgTi	2.86	1.99	7.23
10V2MgTi	9.48	1.85	9.78

*The number in the catalyst symbol denotes the approximate weight percentage of V calculated as V_2O_5

[a] The content of vanadium is calculated in terms of % by weight of V_2O_5

[b] The content of magnesium is calculated in terms of % by weight

The above data in Table 5.1 show that the surface areas of all catalysts are quite similar and relatively low. However, their surface areas slightly increase with increasing the content of vanadium oxide. This similar behavior was reported by [Teratrakoonwichaya (1996)]. It can be seen that the surface areas of catalysts with V/Mg atomic ratio equal to 1/1 and 2/3 (co-5V1MgTi, 1Mg5VTi, 5V1MgTi and 5V2MgTi) are quite the same. Therefore, the sequence of magnesium loading and the content of magnesium seem to have no effect on the surface area of catalyst.

5.1.2 X-ray Diffraction

The crystal structure of all catalysts is characterized by XRD. Figures 5.1 and 5.2 illustrate XRD spectrum of TiO_2 and V_2O_5, respectively. XRD spectrum of V_2O_5 shows three evident peaks at 2θ values of 20.5°, 26.5° and 31°. To compare with 5VTi catalyst as exhibited in figure 5.3, it is found that XRD spectrum of 5VTi shows peaks at the same position as in TiO_2 spectrum. However, the small peaks of crystalline V_2O_5 at the 2θ values of 20.5° and 26.5° are observed.

For V-Mg-O/TiO_2 system, spectra of all catalysts have the 2θ values which belong to TiO_2 (figures 5.4 to 5.9). The crystalline V_2O_5 peaks cannot be detected in 5V1MgTi and co-5V1MgTi (figures 5.4 and 5.5) but they appear at 20.5° and 26.5° in 1Mg5VTi catalyst (figure 5.6). It indicates that vanadium oxide may not form a V_2O_5 crystal structure on TiO_2 support when magnesium is introduced after or simultaneously with the deposition of the vanadia phase onto titania support. This may be explained that vanadium which first deposited on TiO_2 forms a dispersed vanadia species on TiO_2 surface after calcination at 550°C. Though the melting point of pure V_2O_5 is 700°C, when vanadia is dispersed on TiO_2 surface, it can be melted at a lower temperature than bulk V_2O_5. Therefore, after the impregnation of magnesium, the catalyst is then calcined at 550°C and vanadia species can be melted at this calcination temperature and react with MgO to form a new V-Mg-O compound, not form vanadium oxide. For this reason, the crystalline V_2O_5 peaks at 20.5° and 26.5° disappear. The similar phenomenon occurs in the case of co-impregnation of vanadium and mangesium. In contrast, magnesium forms a stable MgO on the TiO_2 suface after the calcination at 550°C when it is first impregnated on TiO_2. The melting point of MgO is about 2800°C thus, after vanadium is impregnated on MgO/TiO_2 and then calcined at 550°C, MgO is not melted at this calcination temperature. Vanadium can not react with magnesium to form V-Mg-O compound but it appears in the forms of crystalline V_2O_5 on the TiO_2 surface. Therefore, the small peaks of crystalline V_2O_5 can be detected in 1Mg5VTi catalyst.

In the case of 5V2MgTi and 3V2MgTi catalysts (figures 5.7 and 5.8), the unobservable diffraction line of V_2O_5 crystal can be explained with the above reason. With increasing V content, 10V2MgTi catalyst as shown in figure 5.9, the small V_2O_5 peaks at 20.5° and 26.5° appear. Its intensity is rather similar to 5VTi. This can be suggested that some parts of vanadium react with magnesium and the excess vanadium forms the crystalline V_2O_5 on TiO_2 surface.

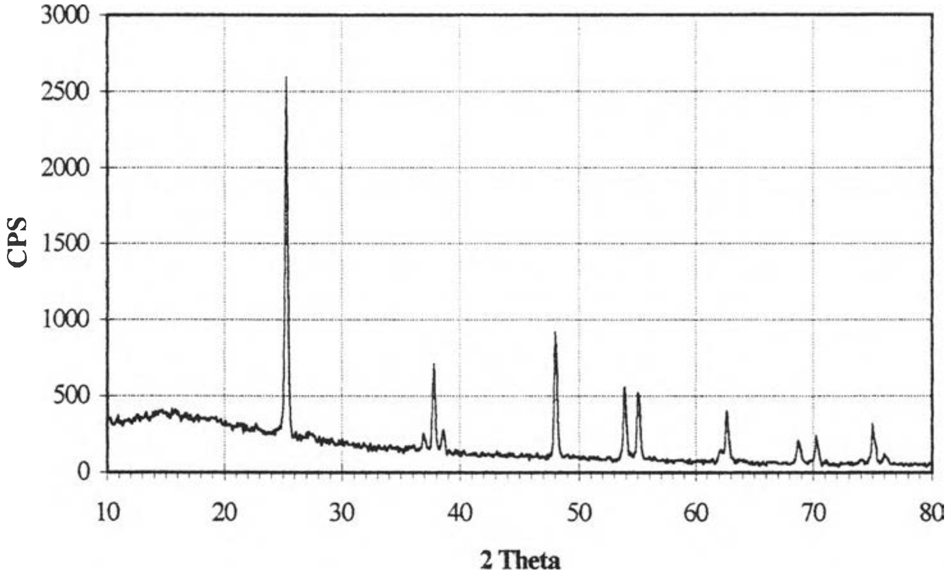


Figure 5.1 X-ray diffraction pattern of TiO_2 catalyst

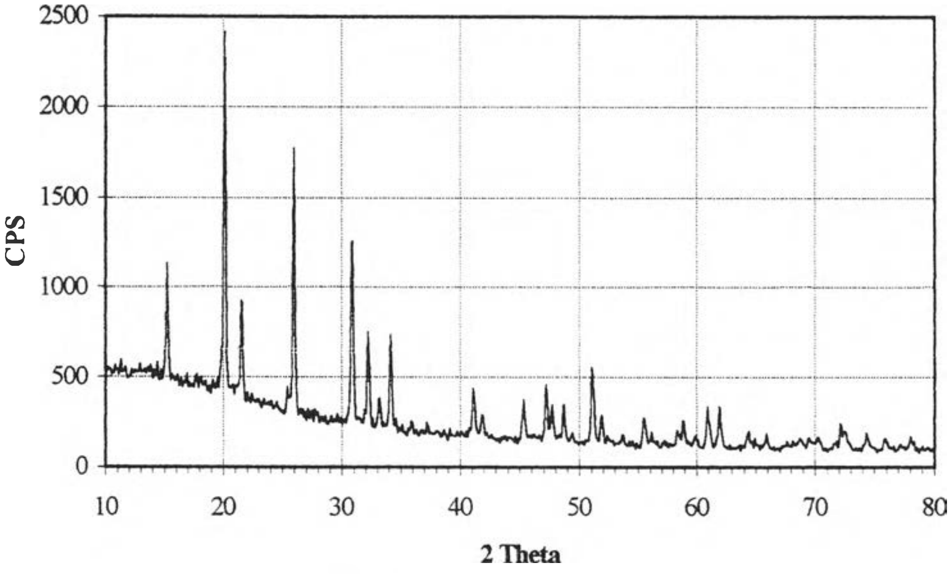


Figure 5.2 X-ray diffraction pattern of V_2O_5 catalyst

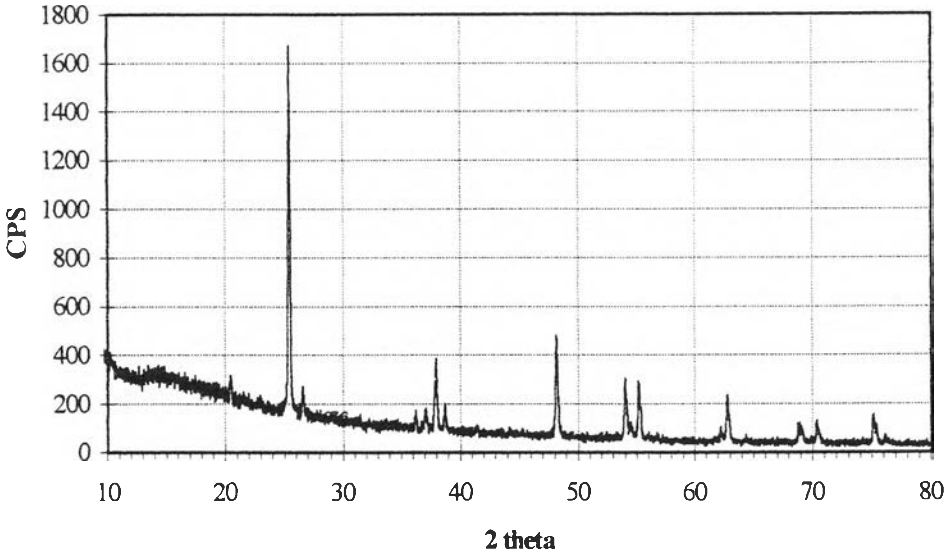


Figure 5.3 X-ray diffraction pattern of 5VTi catalyst

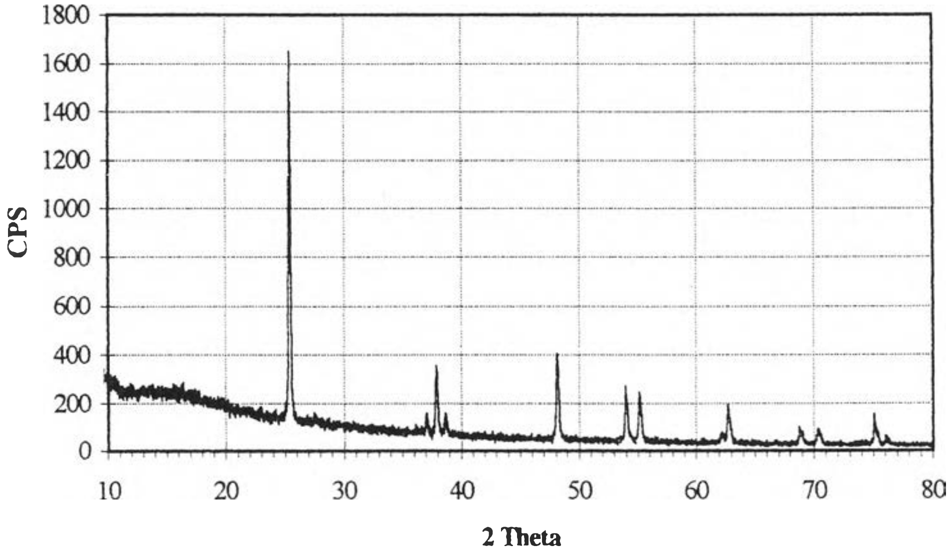


Figure 5.4 X-ray diffraction pattern of 5V1MgTi catalyst

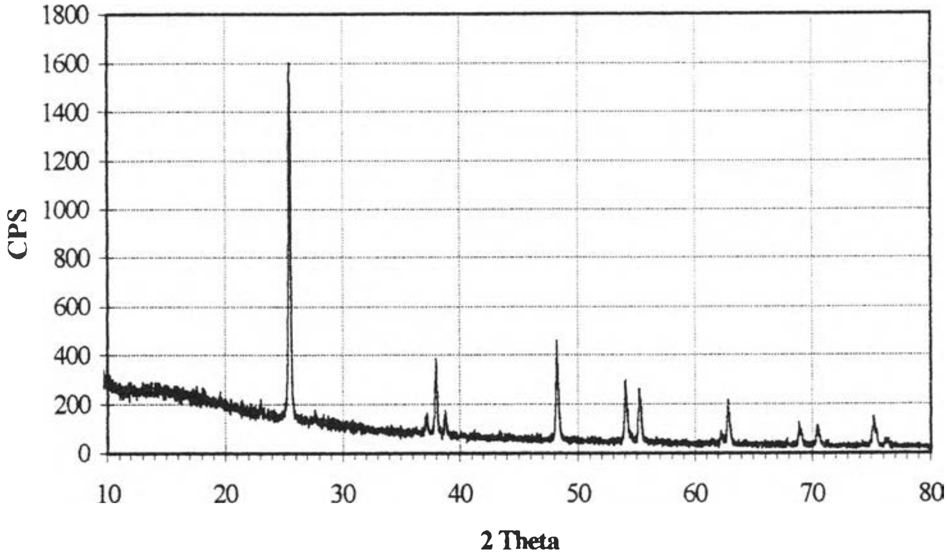


Figure 5.5 X-ray diffraction pattern of co-5V1MgTi catalyst

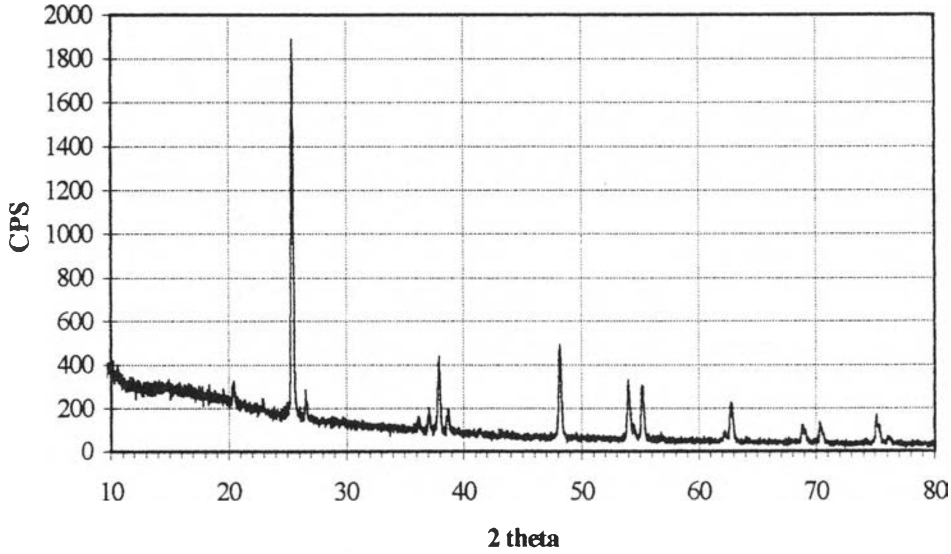


Figure 5.6 X-ray diffraction pattern of 1Mg5VTi catalyst

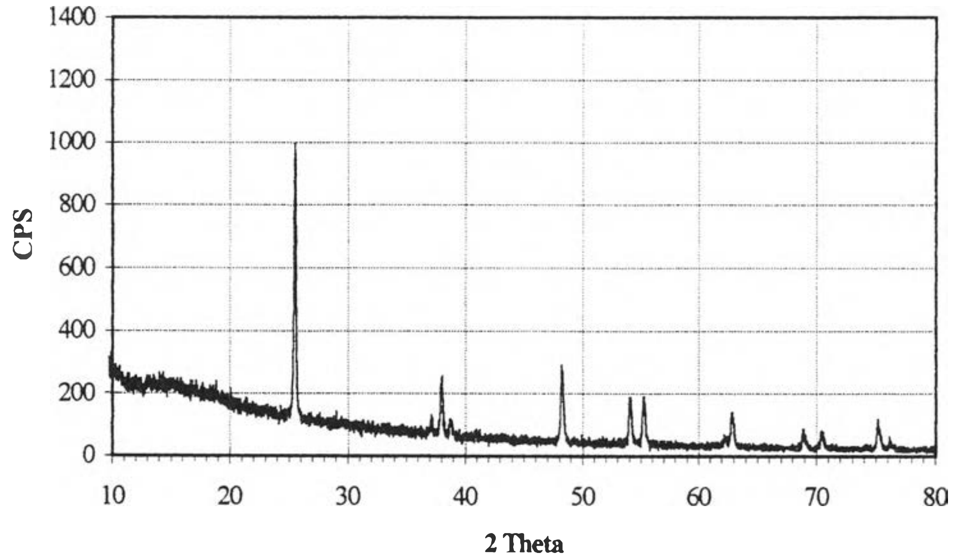


Figure 5.7 X-ray diffraction pattern of 5V2MgTi catalyst

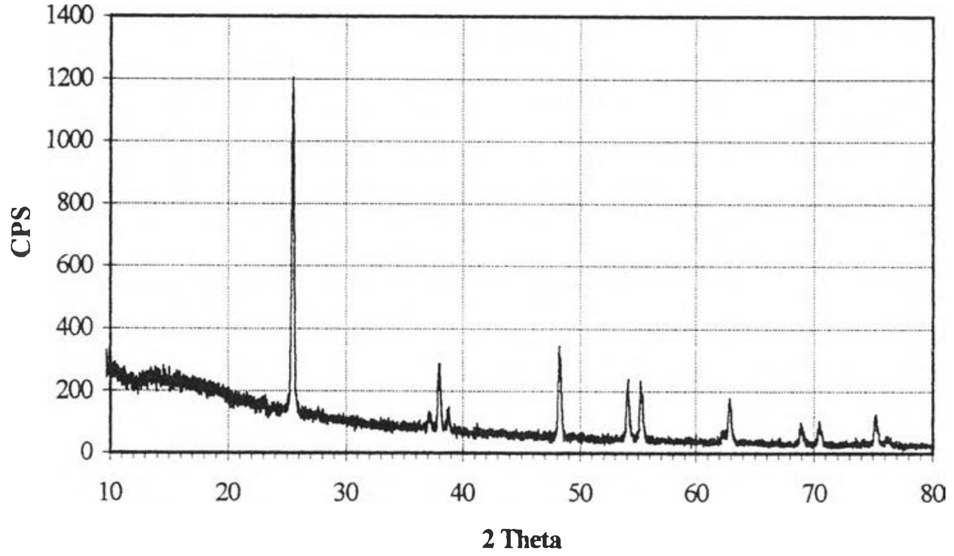


Figure 5.8 X-ray diffraction pattern of 3V2MgTi catalyst

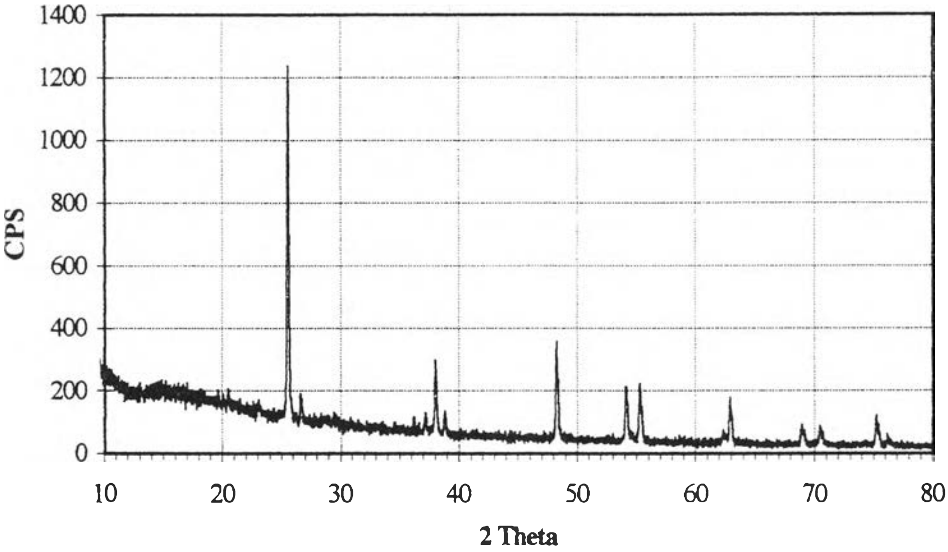


Figure 5.9 X-ray diffraction pattern of 10V2MgTi catalyst

5.1.3 Fourier Transform Infrared Spectrometer (FT-IR)

The infrared radiation in the proper wavelength of 400-2000 cm^{-1} for determining the solid surface is used to identify the functional group on the catalyst surface. Figure 5.10 shows IR spectrum of TiO_2 catalyst. Strong absorption IR bands at 580 and 680 cm^{-1} are observed. The IR spectra of 5VTi and V-Mg-O/TiO_2 catalysts, as presented by figures 5.11 to 5.17, show the absorption bands at the same positions as TiO_2. This can be indicated that the amounts of vanadium and magnesium on TiO_2 surface are much less to observe the changes in IR bands.

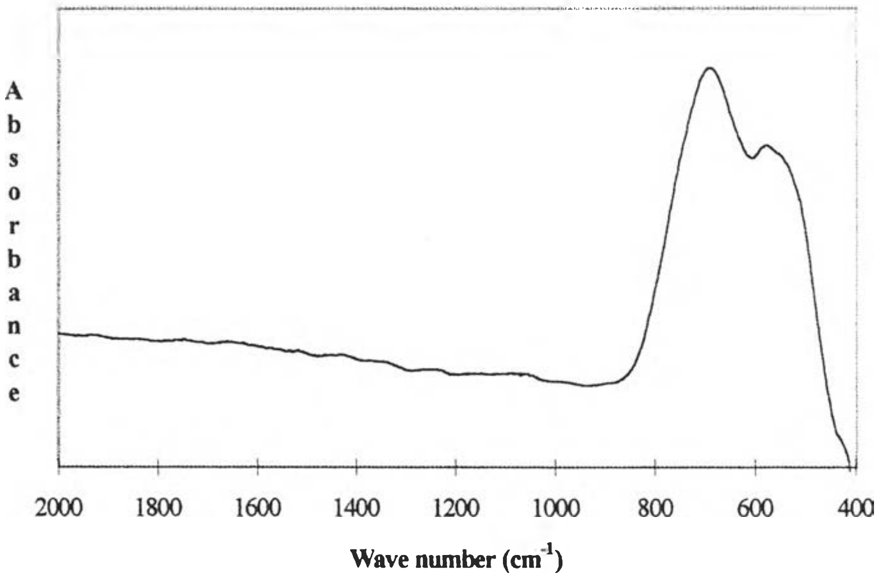


Figure 5.10 IR spectrum of TiO_2 catalyst

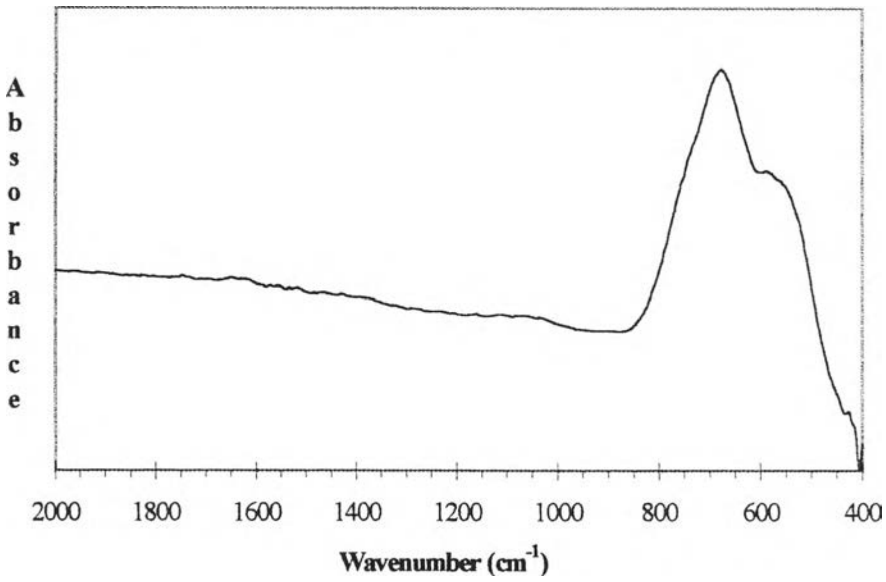


Figure 5.11 IR spectrum of 5VTi catalyst

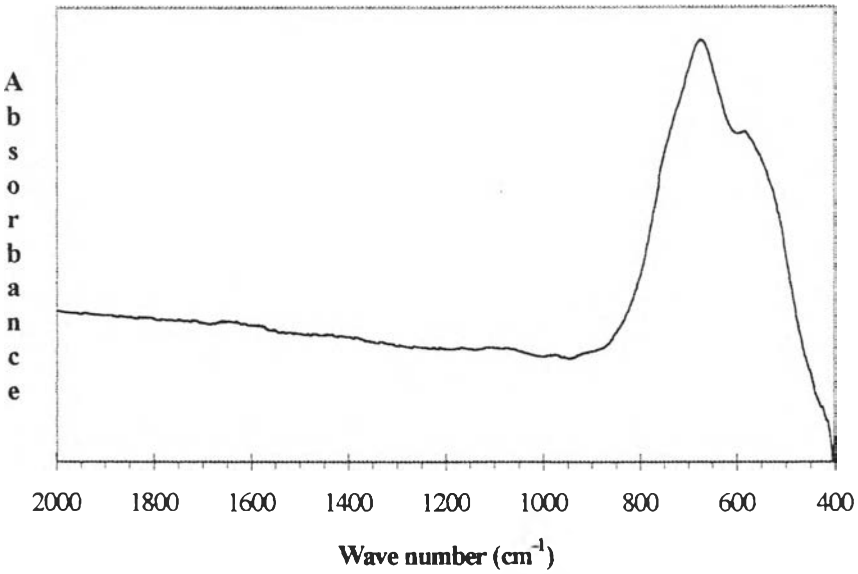


Figure 5.12 IR spectrum of 5V1MgTi catalyst

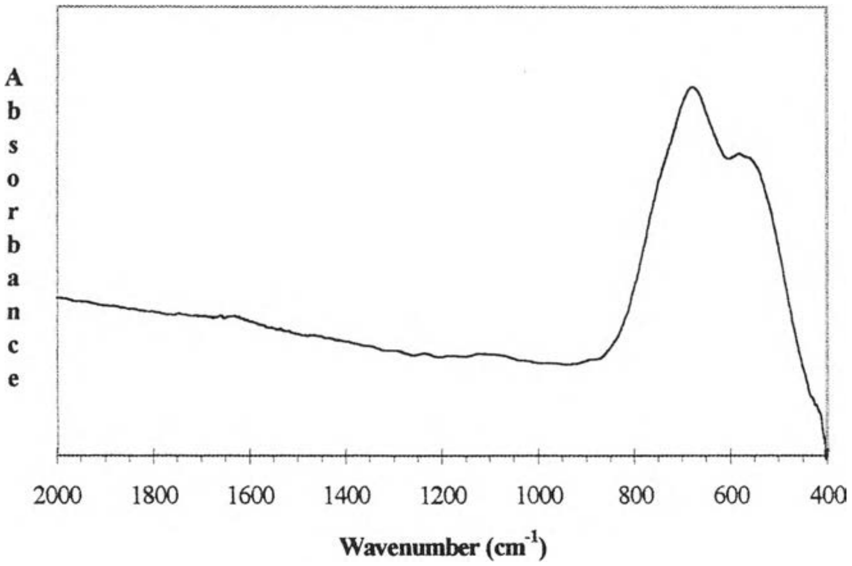


Figure 5.13 IR spectrum of co-5V1MgTi catalyst

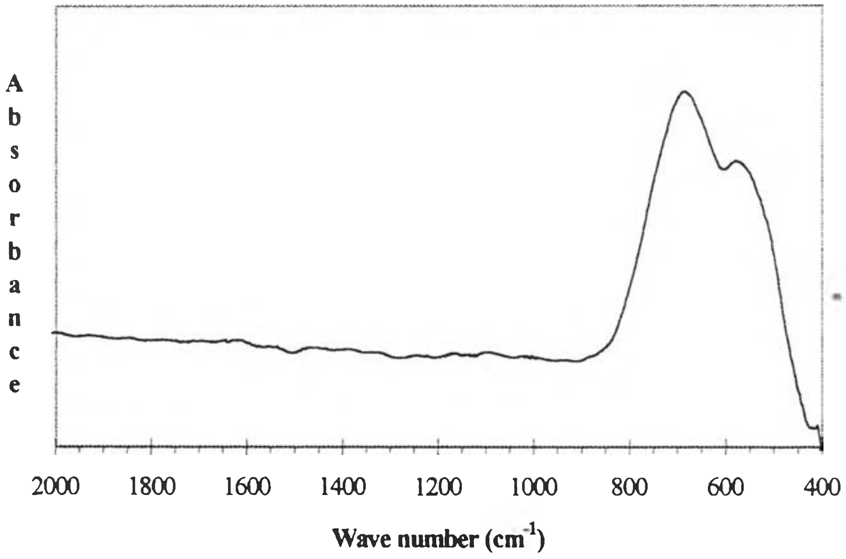


Figure 5.14 IR spectrum of 1Mg5VTi catalyst

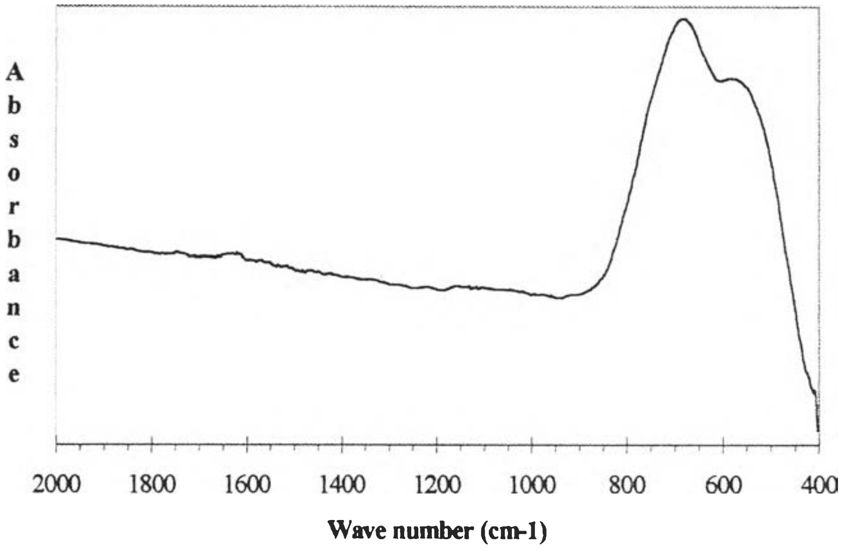


Figure 5.15 IR spectrum of 5V2MgTi catalyst

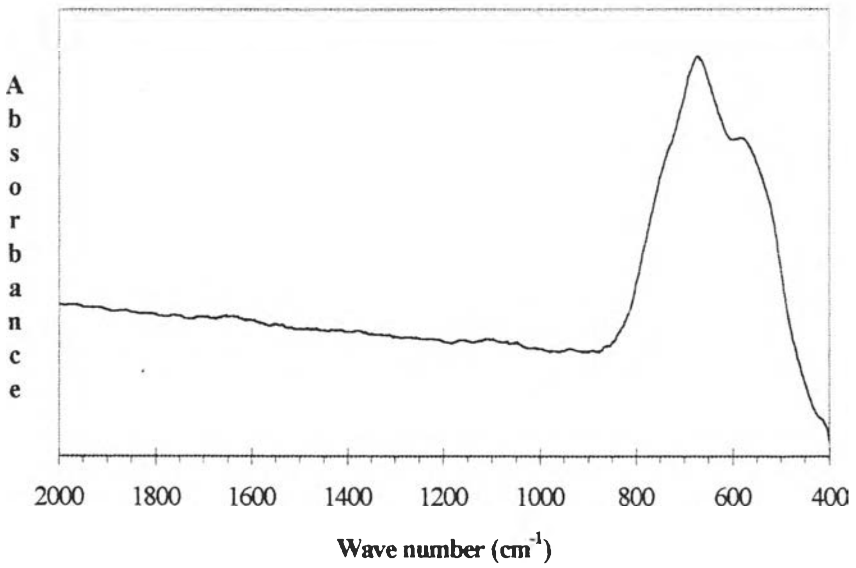


Figure 5.16 IR spectrum of 3V2MgTi catalyst

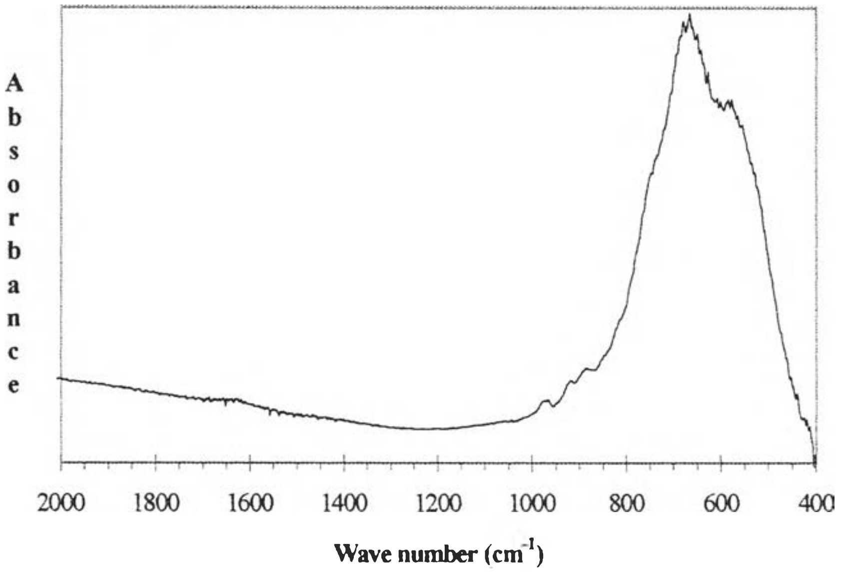


Figure 5.17 IR spectrum of 10V2MgTi catalyst

5.2 Catalytic reaction

In this work, the interaction between vanadium oxide and magnesium/titanium oxide is received much attention. Since V-Mg-O/TiO_2 system is a novel system that has no information about its catalytic property, the following catalytic test reactions are carried out to study the catalytic performance of V-Mg-TiO_2 catalyst.

5.2.1 Propane Oxidation

Because of the simple molecule of alkane, the reaction is not much complicate. Thus propane oxidation is first chosen as catalytic test for V-Mg-O/TiO_2 system. The results of the propane oxidation are discussed below. For all catalysts, the major products are propene and CO_2. Small amounts of methane and ethene are also produced.

The catalytic property of 5VTi catalyst is illustrated in figure 5.18. The activity of the catalyst gradually increases at the beginning of reaction and then rapidly increases to about 12% at 500°C. The main product observed is CO_2 and its selectivity is almost constant at 90% for all reaction temperature. Small amount of propene (~10%) is observed.

The behavior of V-Mg-O/TiO_2 as catalysts for propane oxidation (figures 5.19 to 5.24) is different from that of 5VTi catalyst. These catalysts are relatively inactive for this reaction. Their maximum activities are in the range of 4-7%. However, adding magnesium can improve the propene selectivity with the expense of the activity of the catalysts. The presence of magnesium on the catalyst surface leads to an increase in basicity. The basic catalyst surface has been claimed to improve the alkenes selectivity during the ODH of alkanes [Bhattacharyya *et al.* (1992), Corma *et al.* (1993b) and Owen *et al.* (1992)]. In addition, the effect of sequence of magnesium loading is doubt to have an effect on the structure and then the catalytic performance of V-Mg-O/TiO_2 catalysts. Hence, 5V1MgTi, co-5V1MgTi and

1Mg5VT catalysts are prepared to answer this question. It is found that these three catalysts present the constant product selectivities over the range of reaction temperature. However, 5V1MgTi (figure 5.19) gives the highest propene selectivity, while the selectivity of co-5V1MgTi (figure 5.20) is lower and that of 1Mg5VTi (figure 5.21) is the lowest. The activities of these three catalysts have almost the same trends. For this reason, the sequence which vanadium oxide is first introduced to TiO_2 and then followed by magnesium presents the best catalytic performance. From XRD results, it can be seen that the formation of crystalline V_2O_5 can be observed on 1Mg5VTi catalyst but it is not observed on 5V1MgTi and co-5V1MgTi catalysts. This means that the propene selectivity depends on the structure of the catalyst. Moreover, the crystalline V_2O_5 has been reported to be non-selective catalyst in the oxidative dehydrogenation of propane to propene [Chaar *et al.* (1988), Sam *et al.* (1990)]. This may be the reason why the propene selectivity of 5V1MgTi and co-5V1MgTi is higher than that of 1Mg5VTi.

From the above results, it can be seen that magnesium can promote the propene selectivity of the catalysts. Therefore, the V/Mg atomic ratio is changed from 1/1 in 5V1MgTi catalyst to 2/3 in 5V2MgTi catalyst to study the effect of magnesium content on catalytic property of catalyst. The conversion and product selectivities of 5V2MgTi are demonstrated in figure 5.22. This catalyst also shows rather constant product selectivities. The main product is always CO_2 but the selectivity to propene is enhanced comparing with 5V1MgTi. Propene selectivity increases from 23% on 5V1MgTi to nearly 30% on 5V2MgTi while the propane conversions of two catalysts are quite the same and reach the maximum value about 5% at 500°C.

As mentioned above, the basic catalyst surface can promote the propene selectivity by supporting the desorption of propene from the catalyst surface. 5V2MgTi catalyst has more magnesium content (*i.e.* more basicity) than 5V1MgTi catalyst thus the more basicity of 5V2MgTi will provide the propene selectivity to be better.

To investigate the effect of vanadium oxide content on the oxidation property of V-Mg-O/TiO_2 catalyst, magnesium content is fixed at 2% and then vary the amount of vanadium oxide in the range of 3-10%. Figures 5.23 and 5.24 illustrate the results of catalytic performance of 3V2MgTi and 10V2MgTi catalysts, respectively. Comparing with 5V2MgTi catalyst, 3V2MgTi catalyst (figure 5.23) shows the lowest activity. The absence of both activity and selectivities curves at the reaction temperature between 350-400°C is because of zero conversion at 350°C. When the temperature is higher than 400°C, the activity increases gradually up to 4% at 500°C. With increasing the amount of vanadium oxide, there is an increment of propane conversion. However, the activity of 10V2MgTi (figure 5.24) is slightly higher than 5V2MgTi. While 3V2MgTi shows the propene selectivity lower than that of 5V2MgTi and relatively constant about 22% for all reaction temperature, the propene selectivity of 10V2MgTi presents the different trend from other catalysts. The selectivity to propene rises continuously with temperature from 22% to 40% , while the selectivity to CO_2 drops slowly from 77% to 58%.

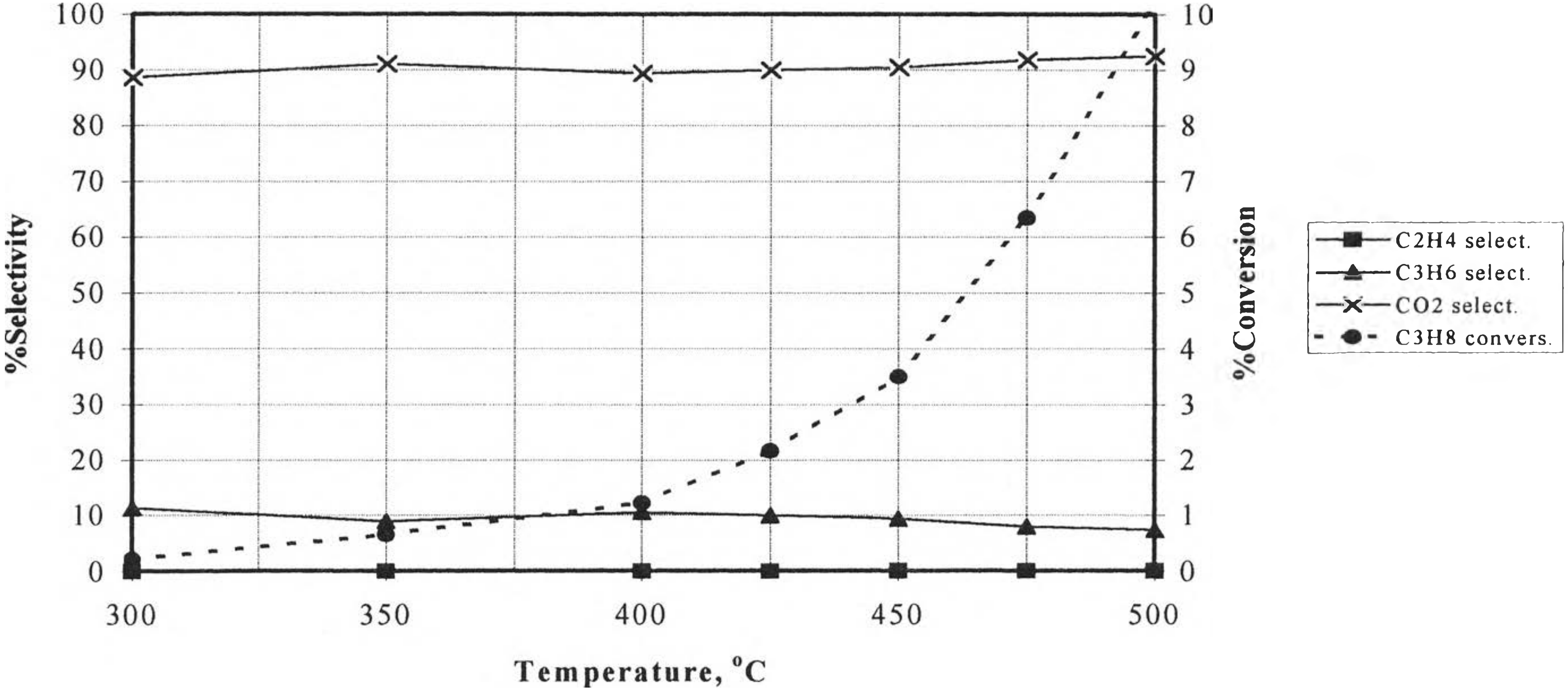


Figure 5.18 Catalytic property of 5VTi catalyst in the propane oxidation

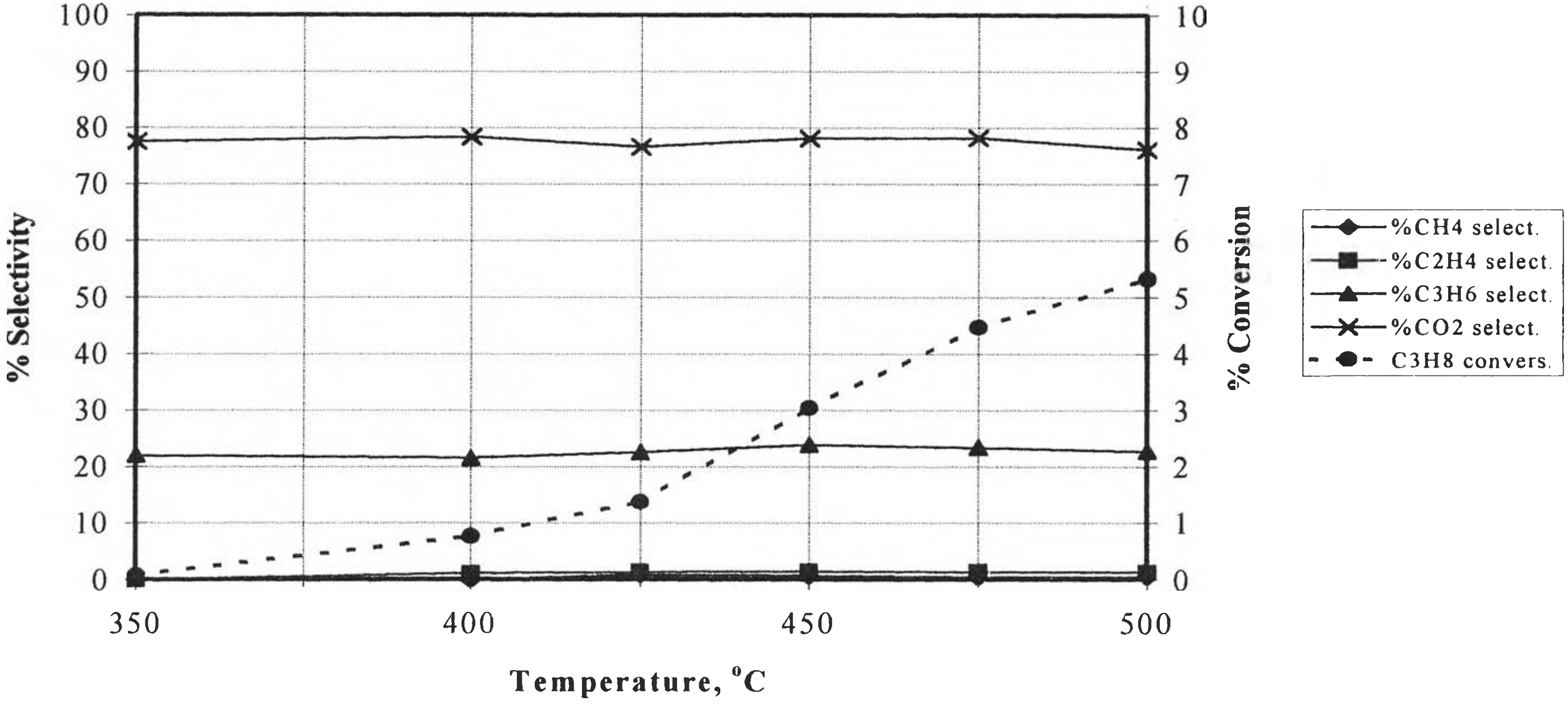


Figure 5.19 Catalytic property of 5V1MgTi catalyst in the propane oxidation

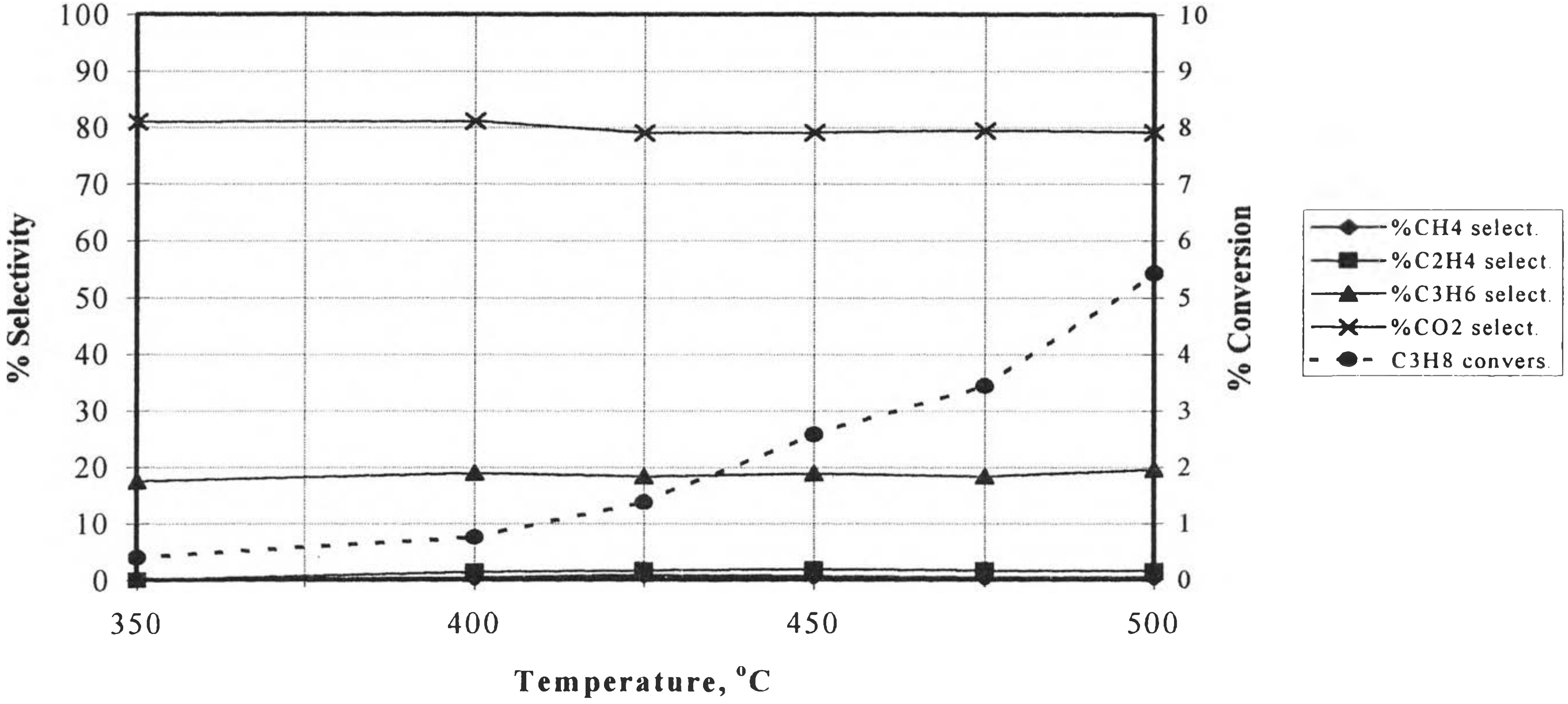


Figure 5.20 Catalytic property of co-5V1MgTi catalyst in the propane oxidation

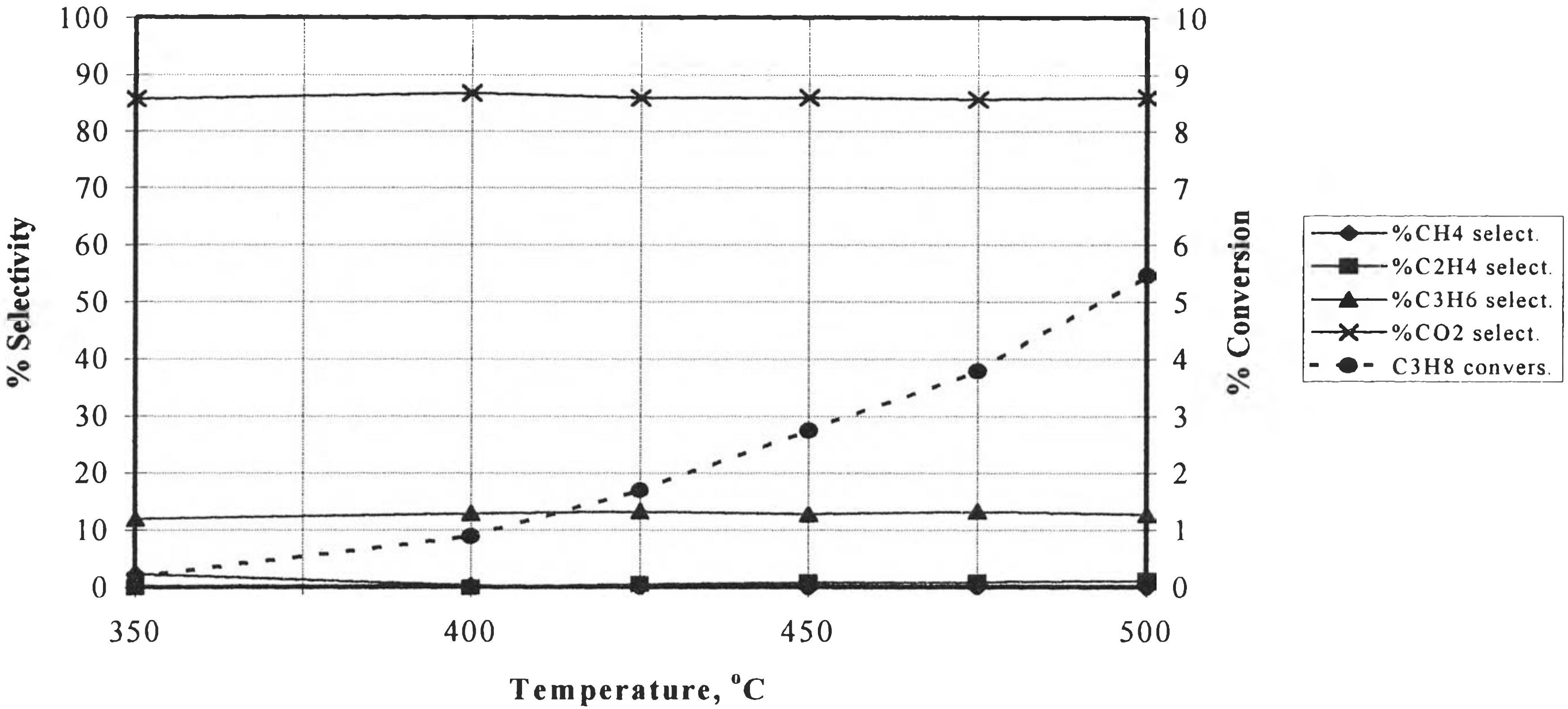


Figure 5.21 Catalytic property of 1Mg5VTi catalyst in the propane oxidation

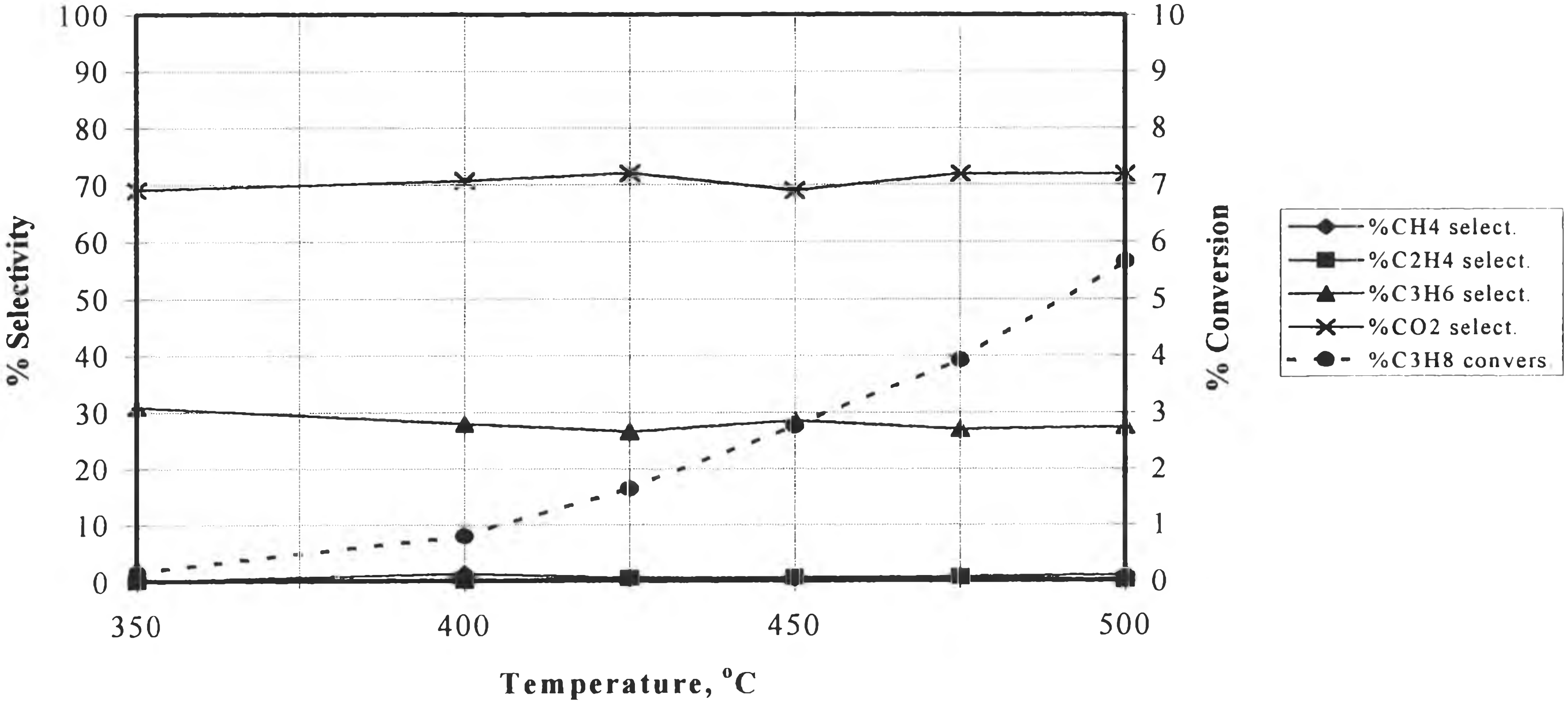


Figure 5.22 Catalytic property of 5V2MgTi catalyst in the propane oxidation

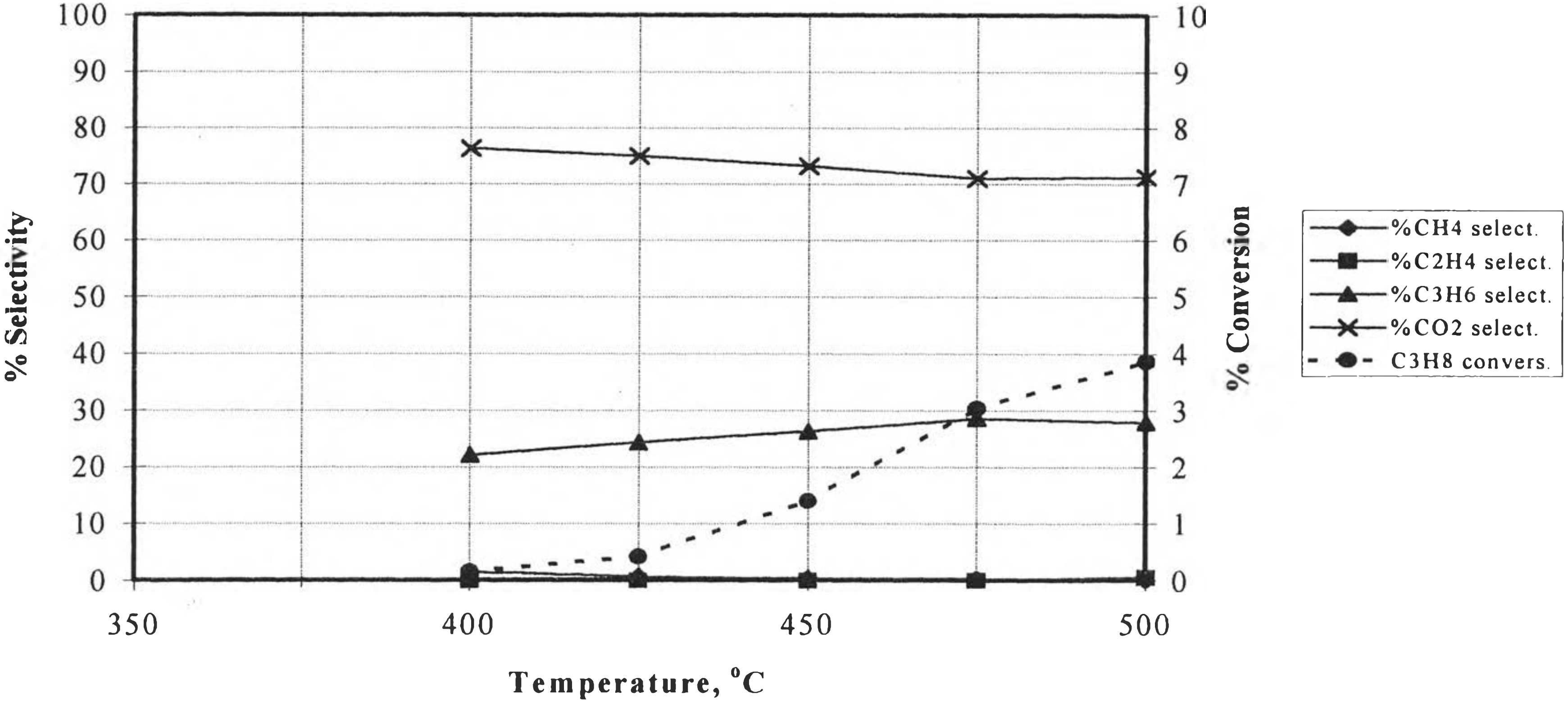


Figure 5.23 Catalytic property of 3V2MgTi catalyst the propane oxidation

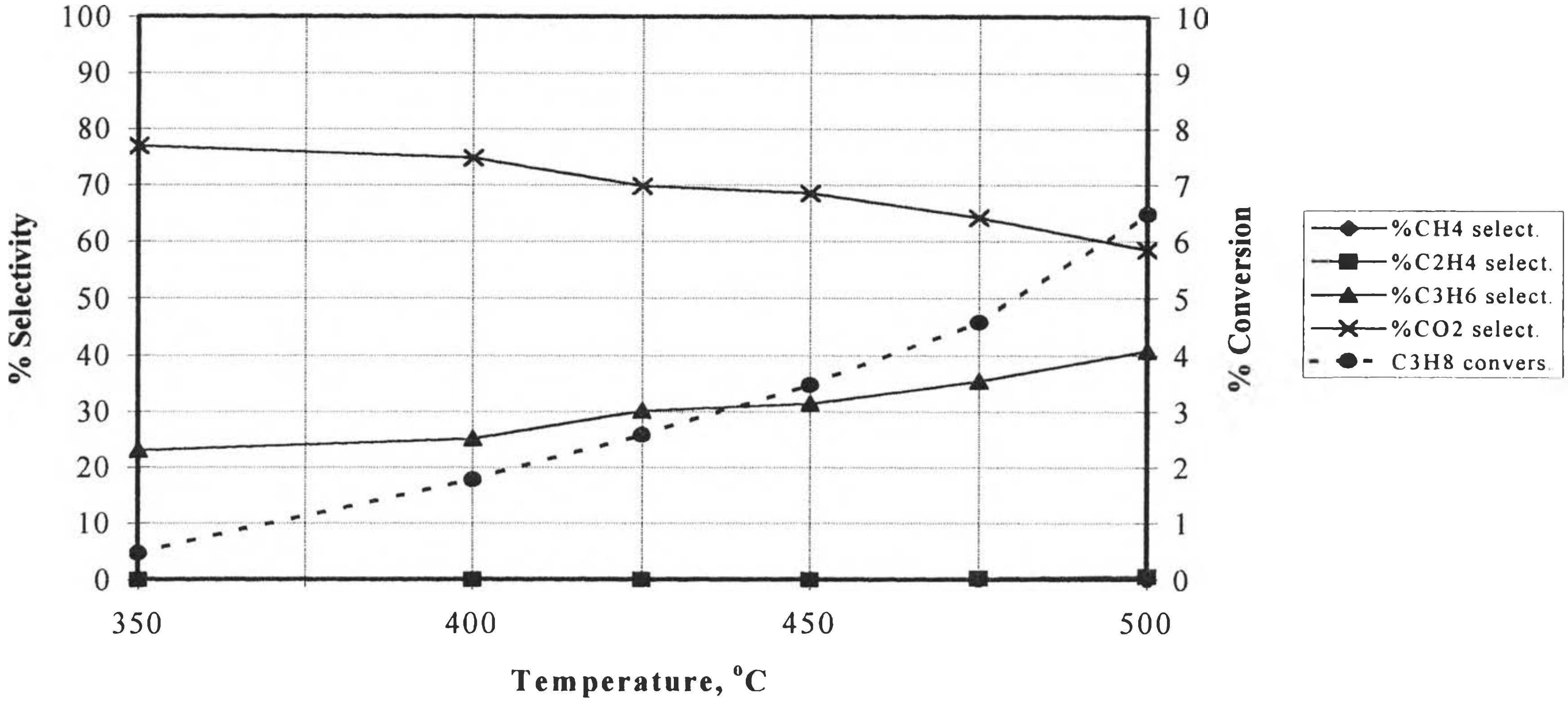
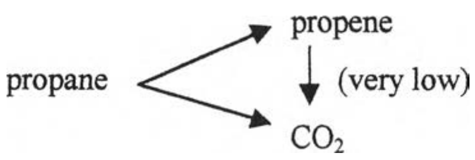


Figure 5.24 Catalytic property of 10V2MgTi catalyst in the propane oxidation

After V-Mg-O/TiO_2 system is tested as catalysts in propane oxidation, it can be concluded that the main useful product obtained from this reaction is propene. Although they seem to be little active for propane oxidation, all of them, except 10V2MgTi, have the benefit of constant propene selectivity, being independent with temperature. Scheme 1 proposes the routes of product formation. CO_2 can be produced via the complete combustion reaction of both propane and propene. However, on V-Mg-O/TiO_2 catalysts, the complete combustion of propene is very insignificant. This indicates that CO_2 formed in this reaction is produced directly from propane. Besides, refers to propene oxidation reaction (section 5.2.3, figure 5.34), V-Mg-O/TiO_2 catalyst is rather inert for propene oxidation over the range of reaction temperature. This confirms that the propene formed in the propane oxidation may not react further to the combustion product, CO_2.



Scheme 1 Routes of propene and CO_2 formation in propane oxidation

In the case of 10V2MgTi catalyst, the trend of the product selectivities is different from the others. Though the propene selectivity is not constant, an increase of temperature does not cause a decrease of propene selectivity. In contrast, the propene selectivity increases while the CO_2 selectivity decreases with increasing the reaction temperature. This phenomenon can be explained by using the following possible hypotheses.

Assuming that the rate of reaction depends on the rate of product adsorption and desorption. The result of 10V2MgTi can be described that at low reaction temperature, propene adsorbs on catalyst surface and oxidizes to form CO_2. When the reaction temperature is increased , this accelerates the desorption of propene from the surface, inhibiting the further oxidation of propene to CO_2. This is the cause of the increase of propene selectivity and the decrease of CO_2 selectivity with increasing the reaction temperature. However, this hypothesis is argued by the result of propene oxidation in section 5.2.3. If this hypothesis is appreciable, propene conversion will be observed and CO_2 will be a detectable product at low temperature and the propene oxidation will be inhibited at high temperature but, in the propene oxidation, the reaction cannot occur at low temperature and very low conversion is obtained at high temperature. Hence, it can be concluded that V-Mg-O/TiO_2 is inactive for reacting propene or propene is less adsorbed on catalyst surface for all reaction temperature. Thus the rates of propene adsorption and desorption at different temperature will not have any effect on the propene selectivity. For this reason, this hypothesis is less possible. The other possible hypothesis is suggested below.

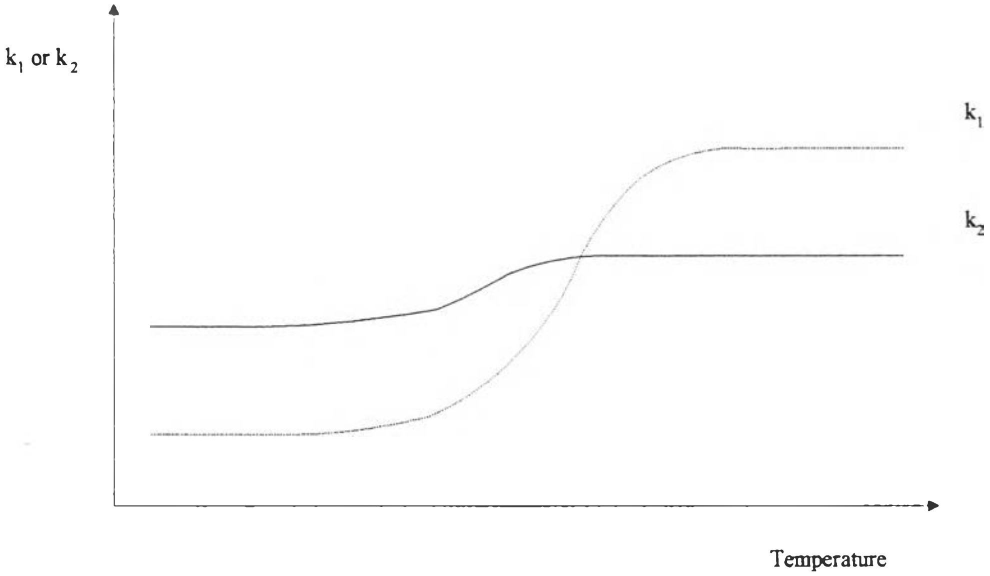


Figure 5.25 Comparison between rate constants of propene formation rate (k_1) and CO_2 formation rate (k_2) at different reaction temperature.

Supposing that this phenomenon is related to the behavior of the rate constants of the rate formation of propene (k_1) and CO_2 (k_2) which is demonstrated by figure 5.26. In this figure the values of k_1 and k_2 at different reaction temperature are compared. At low temperatures, the rate of propene formation is lower than the rate of CO_2 formation (*i.e.* k_1 is smaller than k_2). When the reaction temperature is increased, both k_1 and k_2 are increased but the increase of k_1 is faster than that of k_2. This will result in an increase of propene selectivity with the decrease of CO_2 selectivity in the high reaction temperature region.

In addition, Arrhenius equation: $k_i = k_{i,o}\exp(-\frac{Ea_i}{RT})$ is claimed to support this hypothesis on the basis of first-order reaction. As shown in Arrhenius diagram of 10V2MgTi, figure 5.26, where $\ln(k_1)$ and $\ln(k_2)$ are plotted versus $\frac{1}{T}$ (T is the reaction temperature, K), the plot is linear corresponding to the first-order reaction assumption. It is evident that an increase of reaction temperature causes a more rapid increment of propene formation rate than CO_2 formation rate. Consequently, this hypothesis is appreciable for explaining the results of 10V2MgTi catalyst.

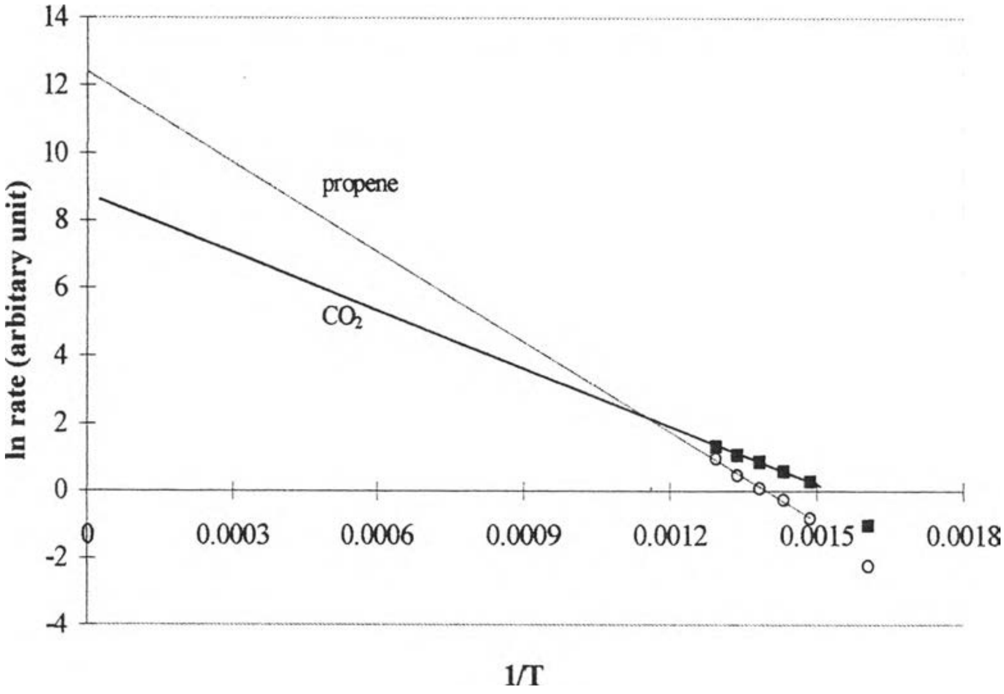


Figure 5.26 Arrhenius diagram between rates of propene and CO_2 formation of 10V2MgTi catalyst

Conclusively, V-Mg-O/TiO_2 system is quite inactive for the oxidation of propane. However, these catalysts have an advantage of constant propene selectivity which is independent from the reaction temperature, especially, for 10V2MgTi catalyst, an increase of reaction temperature can improve the propene selectivity. This characteristic is opposite to V-Mg-O system. Although V-Mg-O catalyst gives high propene selectivity at low reaction temperatures, it declines dramatically when the temperature is higher than 350°C [Kanokrattana (1997) and Thammanonkul (1996)]. This significant fall of propene selectivity is attributed to the further oxidation of propene with oxygen to combustion products such as CO, CO_2 and H_2O at high reaction temperatures. Thus, on V-Mg-O/TiO_2 catalyst, the productivity of propene can be promoted by increasing the reaction temperature. The further investigations for finding the way to enhance the activity of V-Mg-O/TiO_2 catalyst are very interesting.

Moreover, the dispersion of V-Mg-O compounds on TiO_2 surface increases the catalytic performance of V-Mg-O compounds. With comparing between the propene yield per weight of V-Mg-O compounds of 5V2MgTi in this research and that of 28V-Mg-O catalysts in previous researches [Kanokrattana (1997) and Thammanonkul (1996)], it is observed that mole propene formed per mole propane in feed per weight of V-Mg-O compounds of 5V2MgTi is better than that of 28V-Mg-O shown in figure 5.27.

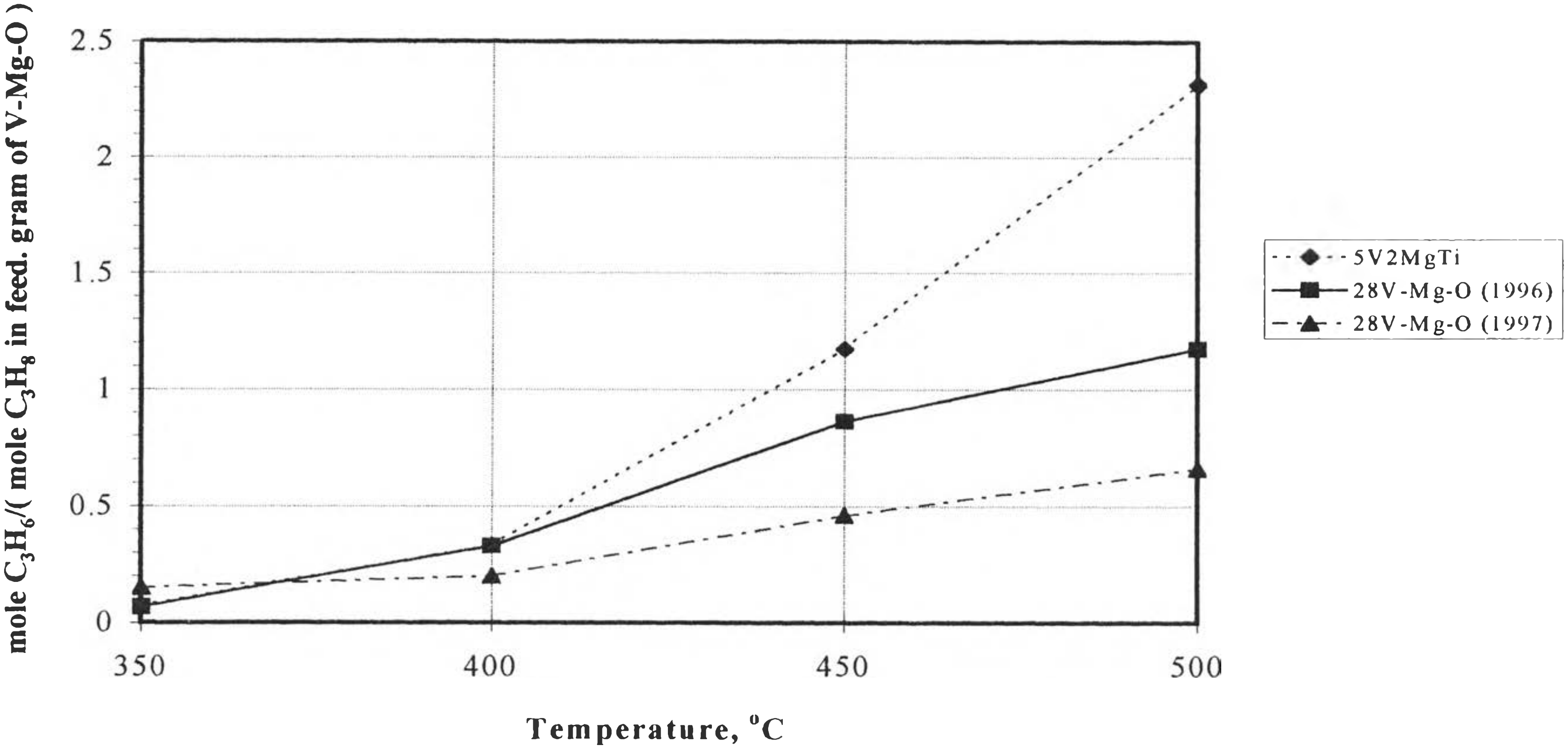


Figure 5.27 Comparison between mole C_3H_6 per mole C_3H_8 in feed per gram of V-Mg-O compounds of 5V2MgTi and 28V-Mg-O catalysts

5.2.2 Propene Oxidation

The behavior of 10V2MgTi as catalyst for propene oxidation is described in figure 5.28. It is observed that this catalyst is inactive in propene oxidation. The conversion becomes measurable at 400°C and very low. Propanal and CO_2 are only the detectable products. Their selectivities are rather constant about 25% and 72%, respectively. In this reaction, the propene concentration in the reactant feed is 4 vol% which is much higher than the propene concentration formed in propane oxidation. This confirms that the propene oxidation will not occur in the propane reaction.

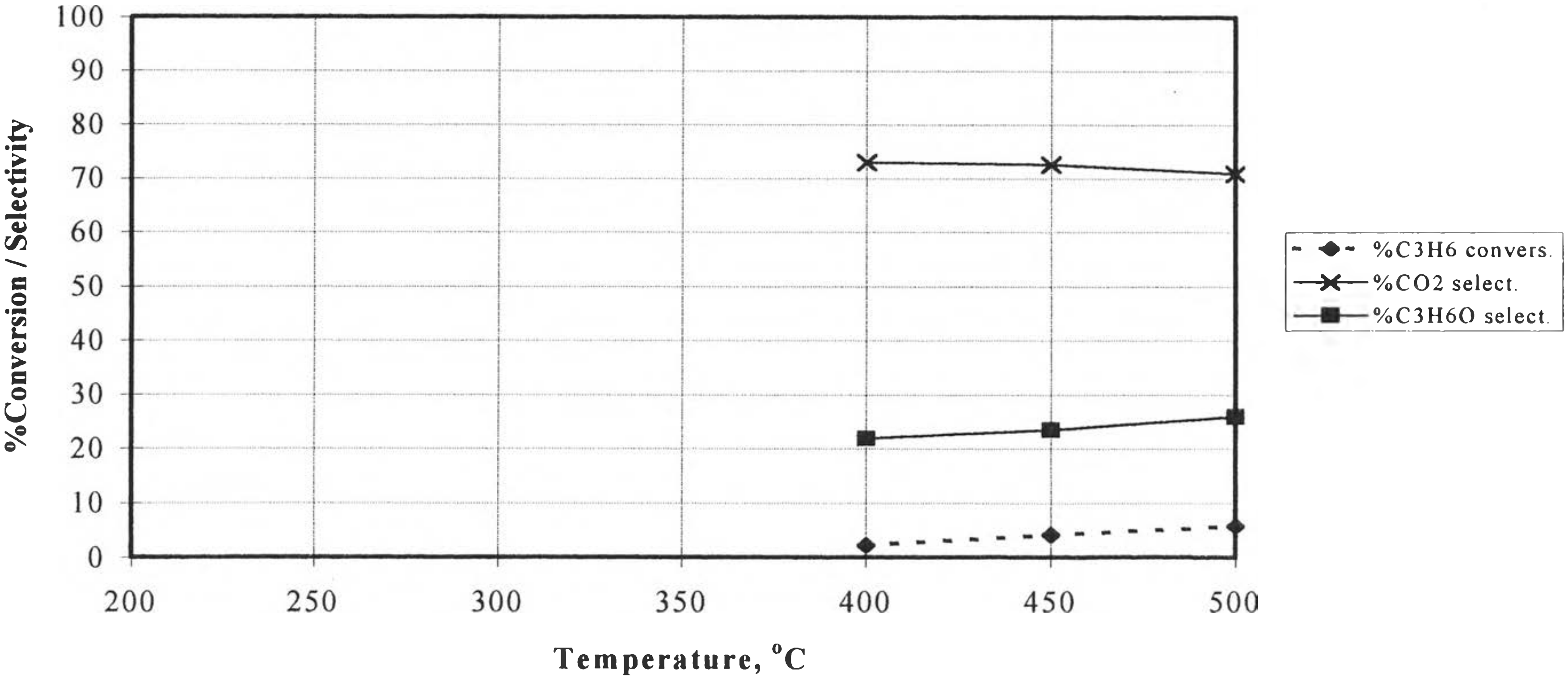


Figure 5.28 Catalytic property of 10V2MgTi catalyst in the propene oxidation

5.2.3 1-Propanol Oxidation

The behavior of the 5VTi as catalyst in 1-propanol oxidation is described in figure 5.29. It is found that 5VTi has very high reactivity in the 1-propanol oxidation reaction. 100% conversion is obtained at reaction temperature near at 250°C. In the beginning (reaction temperature 200-250°C), the selectivities to propene and CO_2 increase rapidly while the selectivity to propanal drops suddenly. At the temperature higher than 250°C, both the propene and CO_2 selectivities increase slightly but the propanal selectivity gradually declines to nearly zero at 500°C. In addition, the selectivity of CO_2 is higher than that of propene for about 2 times.

When mixed oxide catalysts, V-Mg-O/TiO_2, are used in this reaction, the difference of their abilities can be seen as shown in figures 5.30 to 5.35. The results of sequence of magnesium loading are compared in figures 5.30 to 5.32. For 5V1MgTi, as exhibited in figure 5.30, propanal is the main product at low 1-propanol conversion. An increase of reaction temperature causes conversion to approach 100% but selectivity to propanal substantially falls to nearly zero at 450°C while CO_2 selectivity rises to reach a maximum value about 68% at 400°C. After that the CO_2 selectivity drops gradually to 57% at 500°C. In contrast, the selectivity to propene steadily increases over the reaction temperature up to 33%. A broad maximum (11%) in formaldehyde selectivity is observed in the 200-400°C range. Trace of ethene is also detected at high temperature. From figures 5.31 and 5.32, co-5V1MgTi and 1Mg5VTi catalysts have similar catalytic performance as 5V1MgTi catalyst. Subsequently, the effect of magnesium content is also investigated. When the V/Mg atomic ratio is increased from 1/1 to 2/3, there is no impact on the catalytic performance of catalyst. 5V2MgTi catalyst (figure 5.33) presents the same reactivity and selectivities as 5V1MgTi catalyst.

From the above results, it may be concluded that the sequence of introduction of magnesium and the magnesium content have no effect on the catalytic property of V-Mg-O/TiO_2 catalyst for 1-propanol oxidation reaction.

The catalytic tests are then performed on V-Mg-O/TiO_2 catalysts with different vanadium oxide content. These results are summarized in figures 5.33 to 5.35. Considering the activity of these catalysts, they are very active catalysts for this reaction. Their conversions approach almost 100% at 350°C. This means that it is very difficult to compare the effect of vanadium oxide content on the catalyst activity. Therefore, the comparison is performed on their product selectivities. Although 5V2MgTi (figure 5.33), 3V2MgTi (figure 5.34) and 10V2MgTi (figure 5.35) exhibit similar trends as 5V1MgTi, there are some differences. It is observed that the more the amount of vanadium oxide the higher in propene selectivity and the lower in CO_2 selectivity obtained. The selectivity to formaldehyde on 3V2MgTi, 5V2MgTi and 10V2MgTi shows the maximum values at 350°C, 300°C and 250°C, respectively.

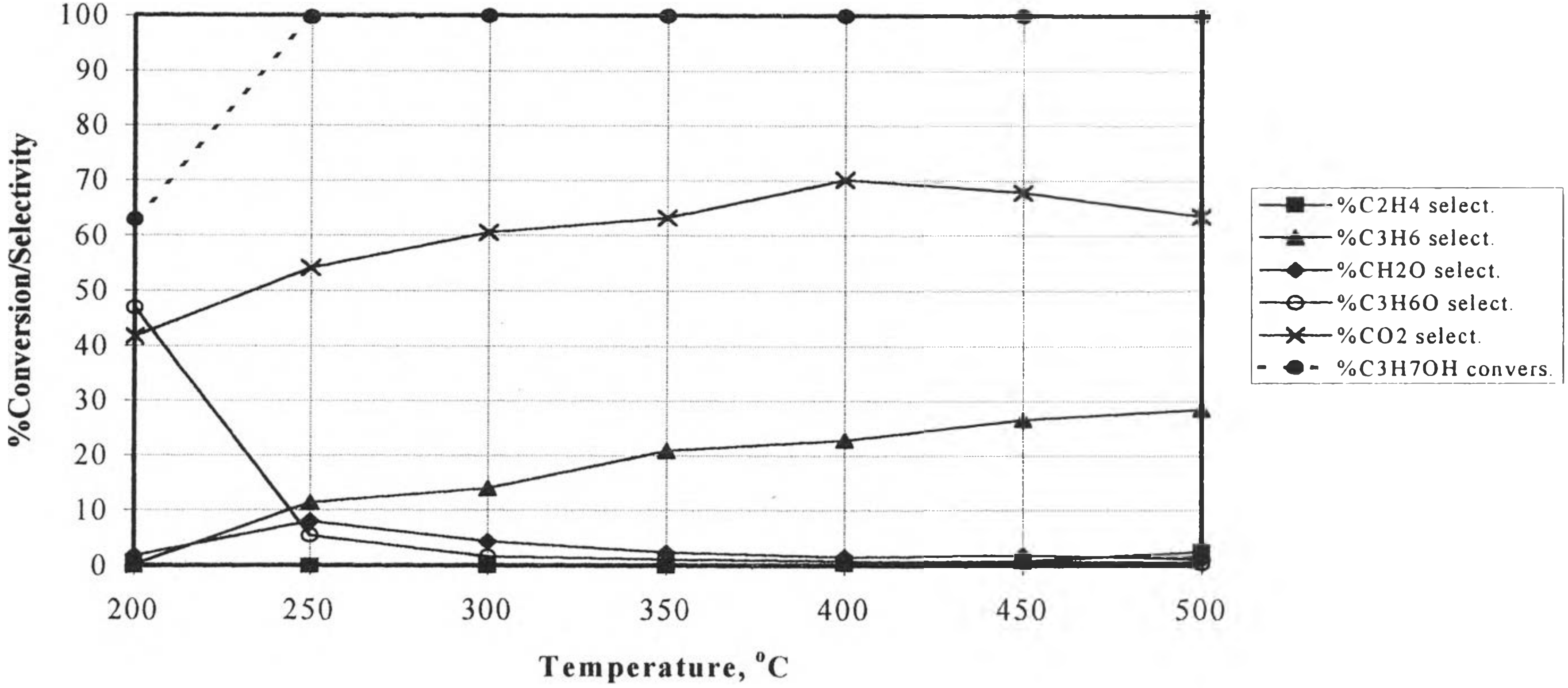


Figure 5.29 Catalytic property of 5VTi catalyst in the 1-propanol oxidation

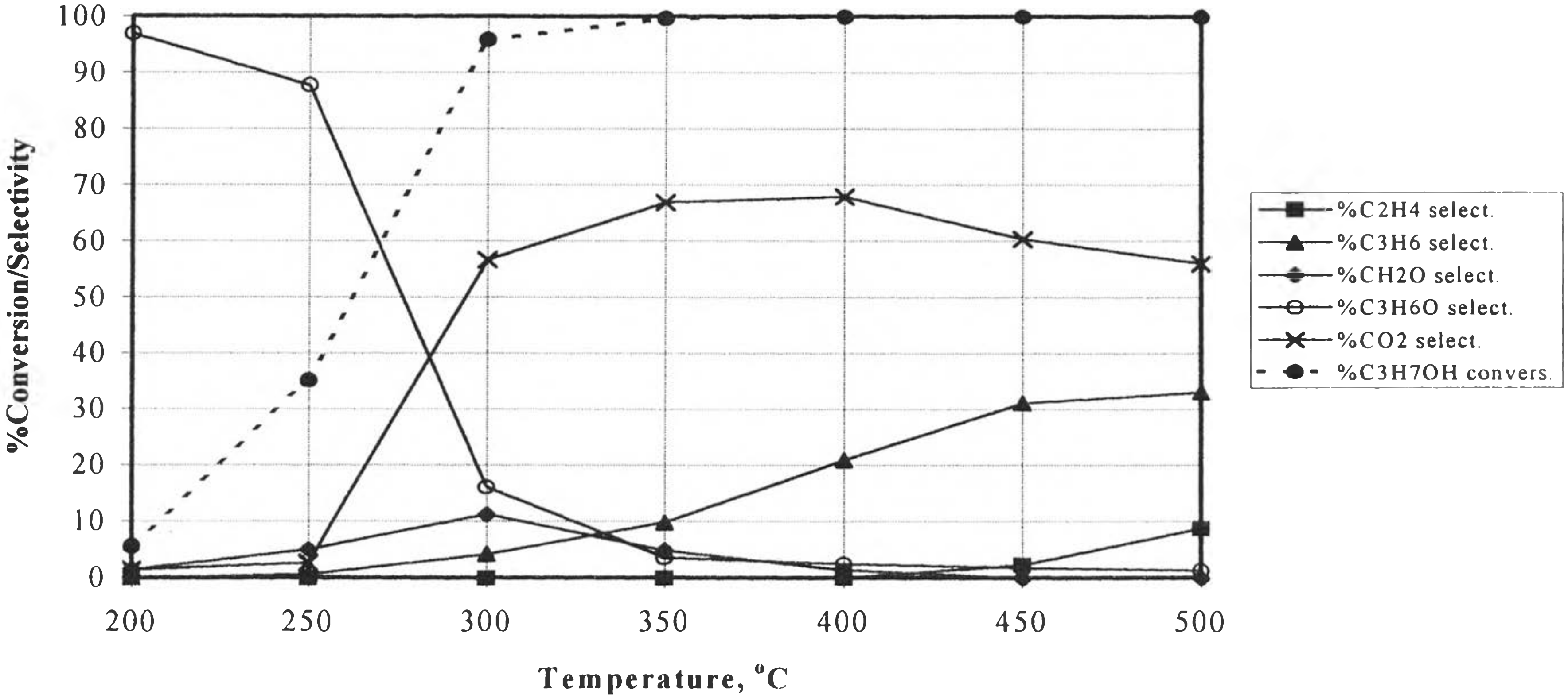


Figure 5.30 Catalytic property of 5V1MgTi catalyst in the 1-propanol oxidation

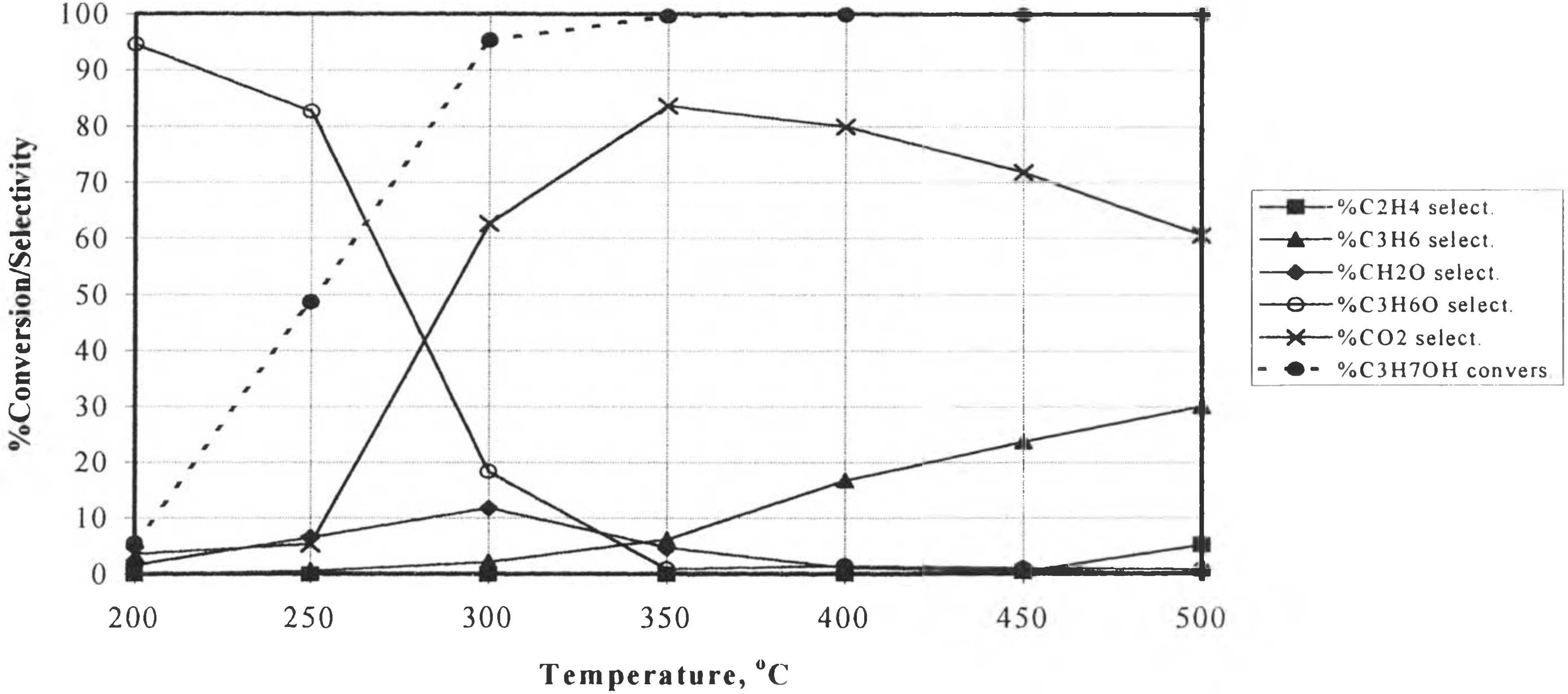


Figure 5.31 Catalytic property of co-5V1MgTi in the 1-propanol oxidation

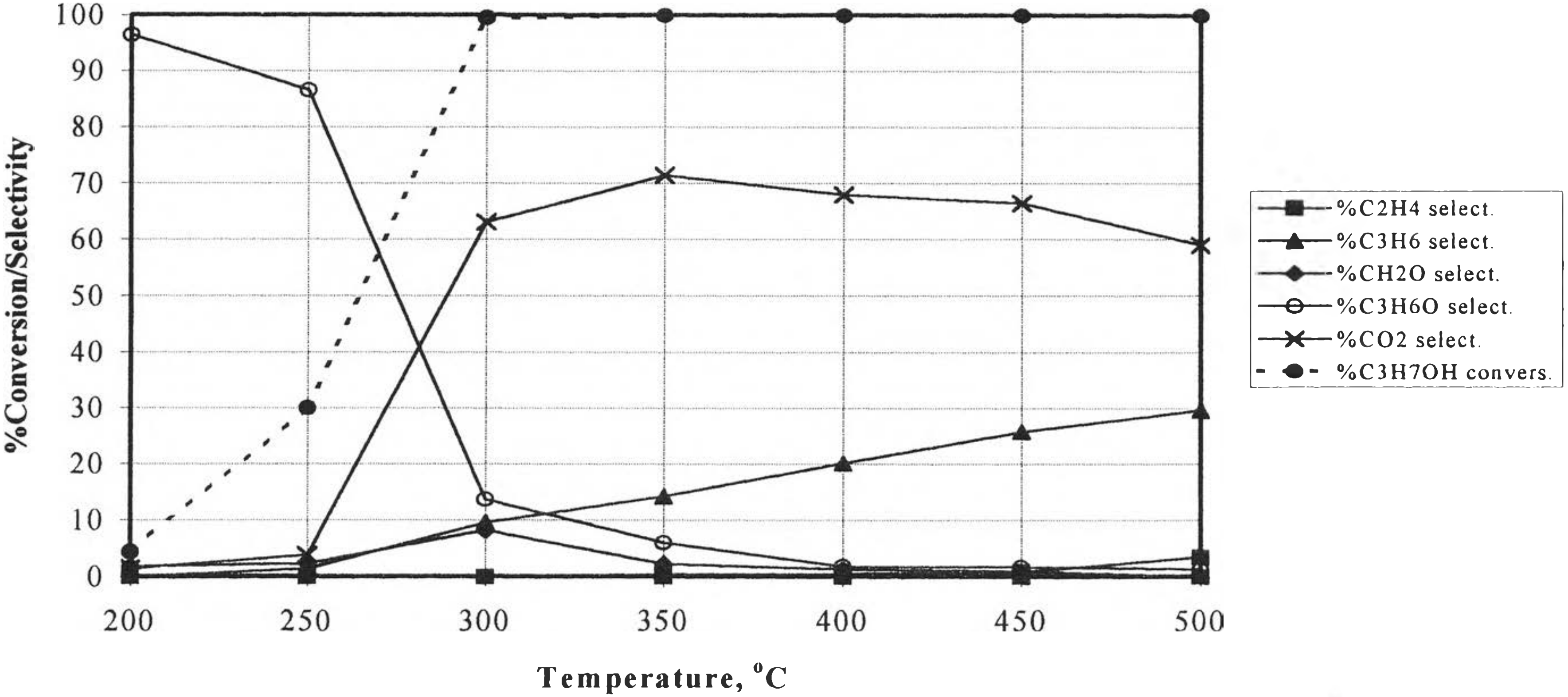


Figure 5.32 Catalytic property of 1Mg5VTi catalyst in the 1-propanol oxidation

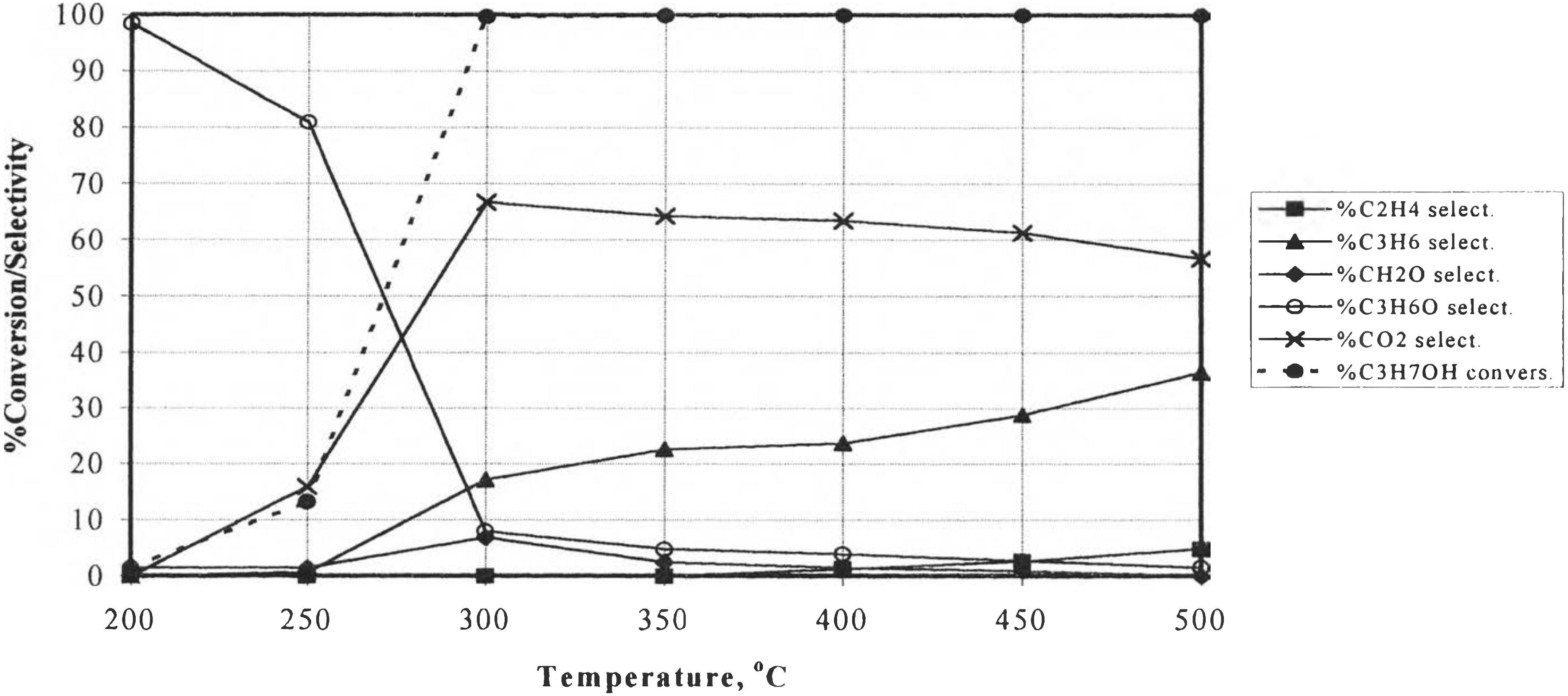


Figure 5.33 Catalytic property of 5V2MgTi catalyst in the 1-propanol oxidation

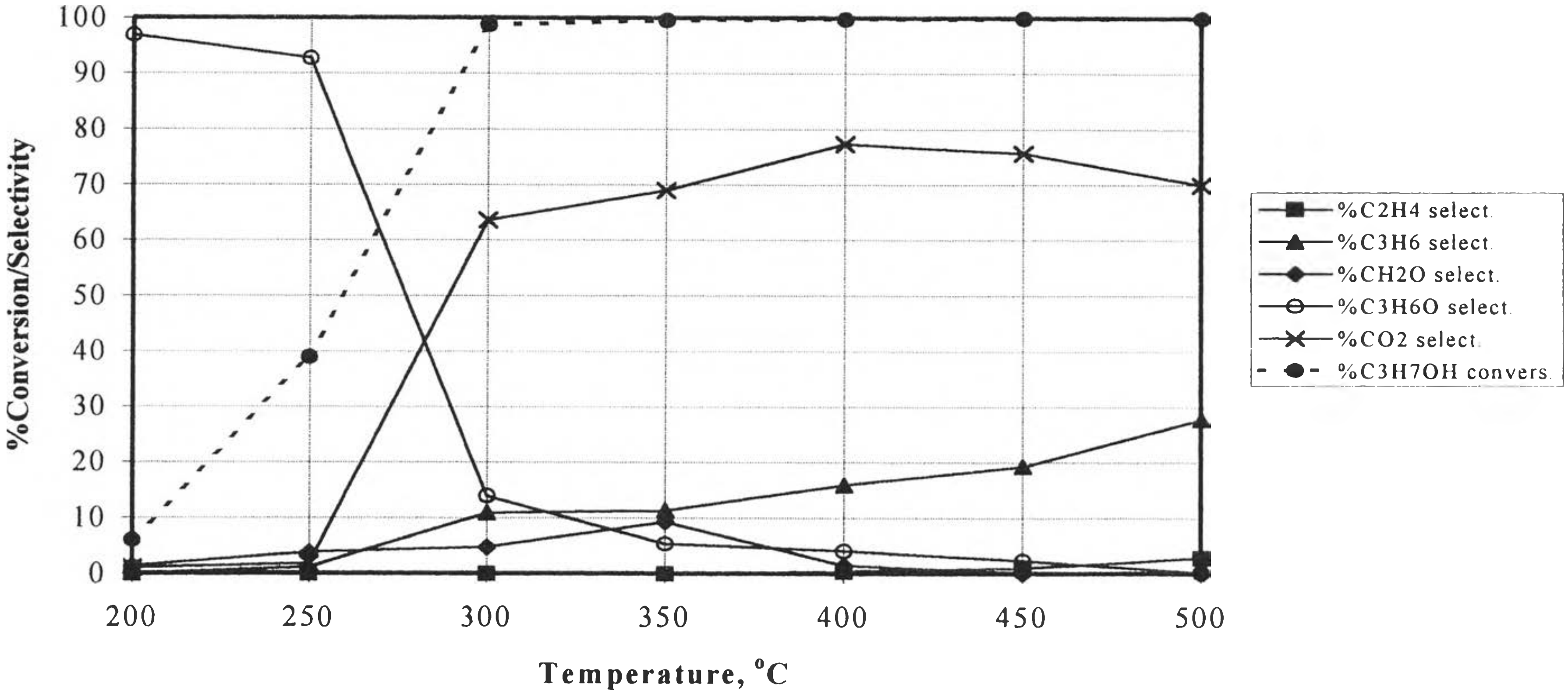


Figure 5.34 Catalytic property of 3V2MgTi catalyst in the 1-propanol oxidation

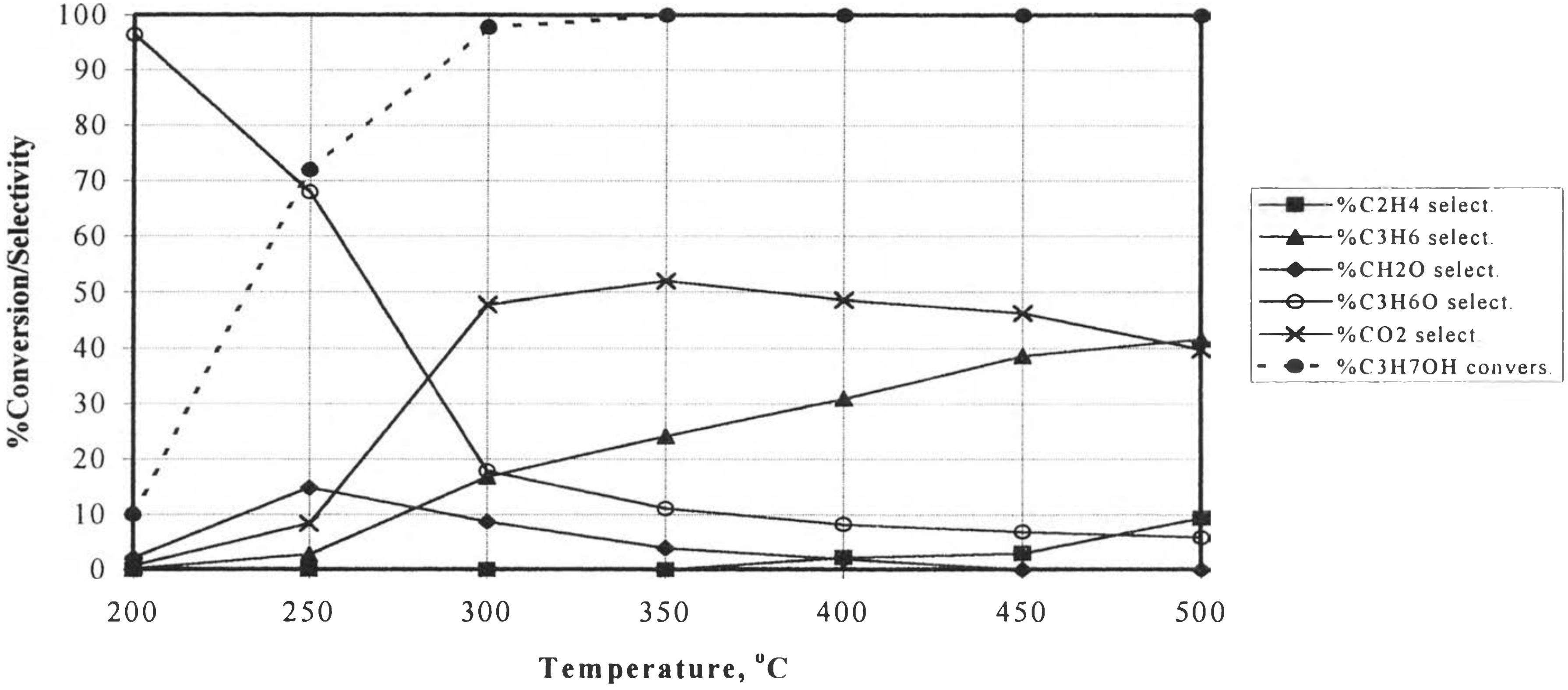
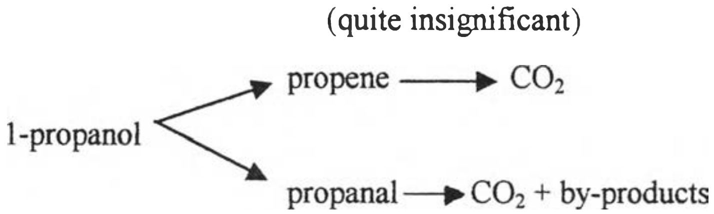


Figure 5.35 Catalytic property of 10V2MgTi catalyst in the 1-propanol oxidation

As seen in 1-propanol oxidation reaction, propanal is the major product at low temperature while propene and CO_2 become significant at high temperature. It can be proposed that propene is produced directly from 1-propanol by dehydration reaction. On the other hand, CO_2 and small amounts of by-products have propanal as an intermediate produced by oxidation reaction from 1-propanol. As mentioned previously, V-Mg-O/TiO_2 catalyst is rather inert to activate propene thus the consecutive reaction of propene to CO_2 is quite insignificant. Scheme 2 presents the routes of product formation in the 1-propanol oxidation.



Scheme 2 Routes of product formation in 1-propanol oxidation

The ability of producing propene from 1-propanol of V-Mg-O/TiO_2 catalyst can be enhanced by increasing the amount of vanadium. It has been known that the dehydration of alcohol requires the presence of acidic sites on catalyst [Morrison and Boyd (1992)]. On V-Mg-O/TiO_2 catalyst, vanadium presents as acidic site. Higher amount of vanadium gives higher number of acidic sites for the dehydration of 1-propanol to propene. Consequently, high propene selectivity is obtained at high vanadium loading.

Furthermore, all V-Mg-O/TiO_2 catalysts show that the selectivity to propene is increased while the selectivity to CO_2 is decreased in the high reaction temperature region. Since the dehydration of 1-propanol to propene is endothermic reaction ($\Delta H_{f\ (1\text{-propanol})}$ = -256.40 kJ/gmol, $\Delta H_{f\ (\text{propene})}$ = 20.42 kJ/gmol) while the oxidation to combustion product, CO_2 is exothermic reaction, the endothermic reaction is preferable at high reaction temperatures. This causes a rise of propene selectivity and a drop of CO_2 selectivity.

According to the above results, it is observed that V-Mg-O/TiO_2 catalyst has the high potential to produce propanal from 1-propanol at low reaction temperature, especially on 3V2MgTi catalyst. At 250°C, the propanal selectivity of 93% at 40% conversion is obtained. The complete combustion and dehydration reactions can be avoided at this temperature because the CO_2 and propene selectivities are very low.

5.2.4 CO Oxidation

10V2MgTi catalyst is also tested in CO oxidation reaction. Figure 5.36 demonstrates that this catalyst is quite inactive because the conversion is relatively low. Since from all of the above reactions, CO is not a detectable product. Therefore, it probably forms in these reactions and progressively oxidizes to form CO_2 or it is not produced in all reactions. The laster is consistent with the result of 10V2MgTi in CO oxidation reaction. Consequently, it can be concluded CO is not formed in propane, 1-propanol and propene oxidation reactions.

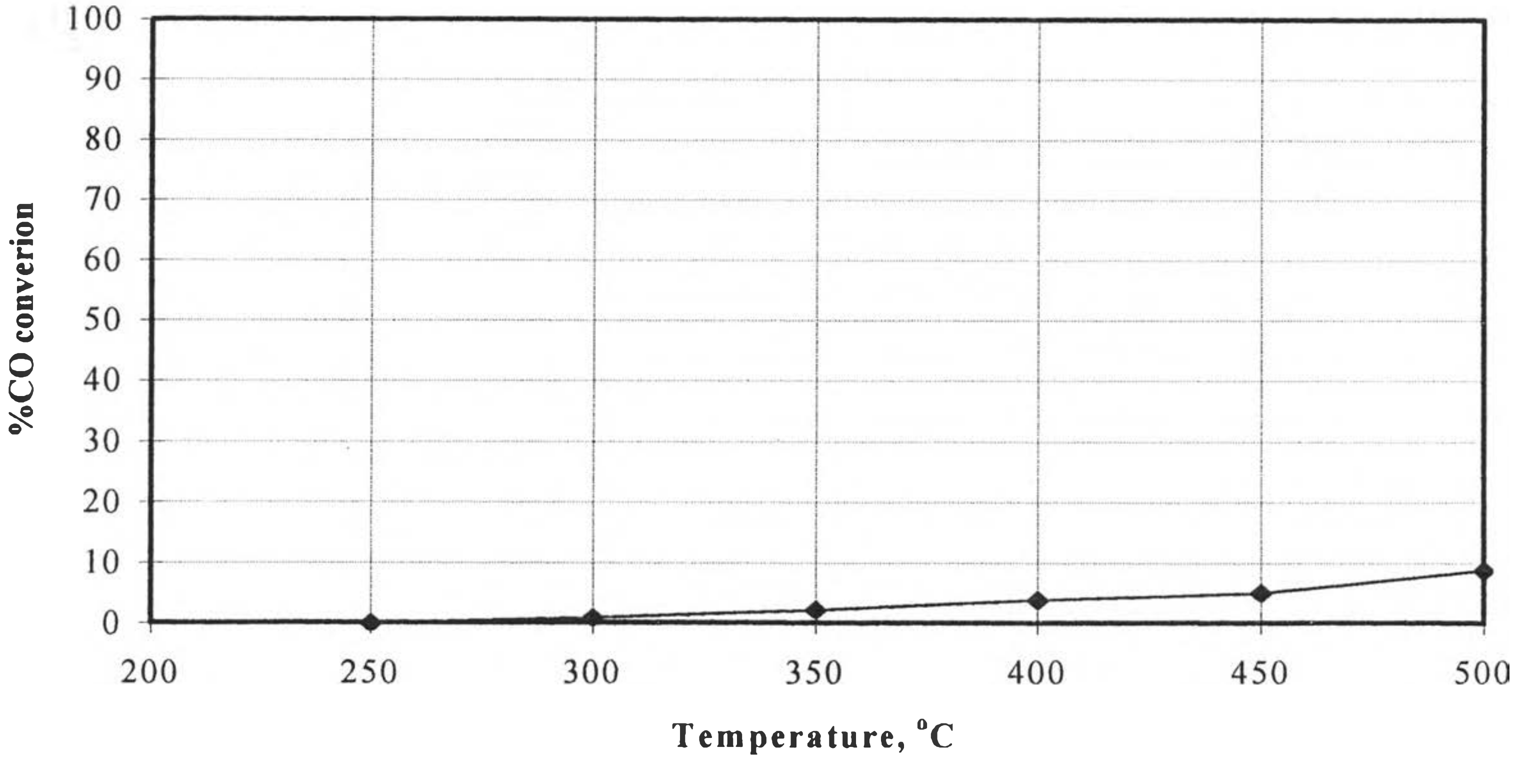


Figure 5.36 Catalytic property of 10V2MgTi catalyst in the CO oxidation