

CHAPTER V

RESULTS AND DISCUSSION

The results and discussion are divided into four parts as follows: catalyst composition and surface area, catalytic test, thermogravimetric and thermal analysis, and catalyst characterization which consists of XRD and IR study.

5.1 Catalyst Composition and Surface Area

5.1.1. Determination of Metal Contents

The metal content of catalysts as measured by AA are shown in Table 5.1 below.

Table 5.1 Chemical compositions of catalysts.

catalyst	%V ^b	%Na ^c	%K ^c
4 ^a V-Mg-O	3.829	-	-
21V-Mg-O	21.199	-	-
28V-Mg-O	28.159	-	-
28V-Mg-O(1%Na)	28.590	1.240	-
28V-Mg-O(2%Na)	28.670	2.130	-
28V-Mg-O(3%Na)	28.680	2.955	-
28V-Mg-O(1%K)	28.118	-	1.126
28V-Mg-O(2%K)	28.340	-	1.976
28V-Mg-O(3%K)	28.322	-	3.130

^a The number in the catalyst label denotes the approximate weight percentage of V₂O₅.

^b The content of vanadium is calculated in term of % by weight of V₂O₅.

^c The content of alkali is calculated in term of % by weight.

5.1.2. Determination of BET Surface Area

Table 5.2 lists surface area of various catalysts used in this research.

Table 5.2 The BET surface area of catalysts

catalyst	surface area (m ² /g.)
MgO	45.51
V ₂ O ₅	8.07
4V-Mg-O	147.56
21V-Mg-O	109.76
28V-Mg-O	97.51
28V-Mg-O(1%Na)	79.78
28V-Mg-O(2%Na)	45.11
28V-Mg-O(3%Na)	49.04
28V-Mg-O(1%K)	87.18
28V-Mg-O(2%K)	82.60
28V-Mg-O(3%K)	63.93

The data show that surface areas of MgO and V₂O₅ are relatively low, especially V₂O₅, when compared to V-Mg-O catalyst. The result illustrates that the surface area of MgO substantially increases with doping a few amount of vanadium on the surface, but it is observable that their surface area decrease with increasing content of vanadium. Chaar et al. [1] has reported a similar behavior. At present, however, no explanation about this phenomenon is reported. Furthermore, the effect of alkali doping on V-Mg-O surface area is also investigated. It can be seen that the surface area of V-Mg-O is reduced sharply by alkali doping. Na seems to have greater effect than K. The effect of alkali content on catalyst surface area is

similar to the effect of vanadium content, i.e. catalyst surface area decrease with increasing content of alkali metal.

5.2 Catalytic Test

Figures 5.1-5.12 show some typical results of the oxidative dehydrogenation of propane on blank, MgO, V₂O₅ and V-Mg-O catalysts. The major products were propene, CO and CO₂. Small amounts of C1 and C2 were also produced.

5.2.1 Catalytic test on blank, MgO and V₂O₅

The result of blank test run is illustrated in Figure 5.1. It can be seen that for empty reactor, the conversion of propane and the selectivity to propene increased slightly from 0 to 10% and from 0 to 25% respectively with increasing temperature from 300 to 600°C. The result of catalytic test on MgO shown in Figure 5.2 is also similar to blank run, but both conversion of C₃H₈ and the selectivity to C₃H₆ are slightly lower in the temperature range of 300-550°C. The conversion and propene selectivity increase significantly from 5 to 33% and 12 to 37% respectively when the reaction temperature is over 550°C. The selectivity to C1 and C2 products also increase significantly. Therefore, it can be concluded that the homogeneous reaction occurs in the beginning of the ODH reaction. However, yield of propene is still low, hence it can be concluded that MgO is rather inactive and non-selective in ODH reaction. The result (shown in Figure 5.3) demonstrates that V₂O₅ is also a non-selective catalyst for ODH reaction. It can be seen that the reaction can start at temperature as low as 300°C. While the conversion increases slightly from 5 to 7%, the selectivity to propene increases more rapidly from 3 to 17% in the temperature range of 350-500°C. But over 500°C, the conversion

increases rapidly to 17% while the selectivity increases much slower to 24%. Small amounts of C1 and C2 were also produced at high temperature. The explanation for this may be that the deep oxidation which does not much occur at low temperature becomes significant at high temperature.

5.2.2 Effect of Vanadium Content

When mixed catalysts, V-Mg-O, were used in this reaction, the difference of their ability to react can be seen clearly as shown in Figures 5.4-5.6. For the lower content of vanadium, 4V-Mg-O, Figure 5.4 shows its catalytic behavior that is similar to MgO but 4V-Mg-O slightly more active than MgO at low temperature. At 600°C the propane conversion reaches the similar value (35%) as MgO. However, its propene selectivity and yield of propene are less. Small amount of C1 and C2 products are also produced at high temperature. Figure 5.5 shows the ability of 21V-Mg-O. It was found that 21V-Mg-O had much more reactivity than MgO and 4V-Mg-O. The conversion increases slowly from 6 to 20% in the beginning of reaction (300-400°C), but the selectivity to propene increases more rapidly from 3 to 32%. After that (400-450°C), the selectivity to propene decreases rapidly to 20% while propane conversion increases to 51% at a more rapid rate than at the beginning. There is a maximum value (around 32%) of selectivity to propene around the temperature of 400°C. In the temperature range of 450-600°C, the selectivity to propene decreases slightly to 17% while the conversion of propane increases slowly to 78%. The amount of C1 and C2 products are produced at around the temperature range of 550-600°C

In the same condition with the above mentioned catalysts, 28V-Mg-O has also been investigated in oxidative dehydrogenation. The extrapolation curve in Figure 5.6 illustrates that the very high maximum selectivity to propene (over 78%) is obtained at nearly zero conversion. After that the selectivity decreases rapidly

from 78 to 29% at 500°C and then it slightly drops to 25% at 600°C. For propane conversion, it increases rapidly to 55% at 500°C. After this temperature, it increases gradually to 67% at 600°C. The absence of the selectivity curve which link propene selectivity between temperature of 300-350°C is attributed to that the selectivity is not defined because of zero conversion at 300°C. Moreover it can be seen that propene selectivity decreased with increasing conversion on V₂O₅, 21V-Mg-O and 28V-Mg-O. The products of C1 and C2 obtained at high temperature are produced in nearly equal amount (around 5%) over V-Mg-O catalysts.

It is observed that the ODH reaction over V-Mg-O catalysts begins at around 350°C.

Figure 5.7 shows a repeated run over 28V-Mg-O under the same condition for proving the repeat ability of the experiment.

The stability of V-Mg-O is also investigated (Figure 5.8), it demonstrates that the selectivity to propene and propane conversion are relatively constant during 4 hours of holding at 550°C.

5.2.3 Effect of Alkali Doping

Figures 5.9 to 5.12 show the effect of doping of various alkali metals (Na and K) onto mixed catalysts on the selectivities to propene and other products (C1, C2) and the conversion of propane.

Figure 5.9 shows the activity and selectivity of 28V-Mg-O(3%Na). The figure demonstrates that there is a relative constant selectivity (around 30%) to propene in the temperature range of 350-500°C. After 500°C, the selectivity gradually decreases to 8% and the propane conversion increases with increasing temperature to 93% at 600°C. Selectivities to C1, C2 are 24% and 16% respectively at 600°C (at high conversion).

28V-Mg-O(3%K) is also investigated and the result is shown in Figure 5.10. The figure demonstrates similar result to that of 28V-Mg-O(3%Na), but higher propene selectivity and propane conversion are obtained. It can be seen that the selectivity to propene is much less than the simple 28V-Mg-O at low temperature and the selectivity to propene decreases slightly from 45 to 37% in the temperature range of 350-500°C, then it trends to be much lower. Moreover, the conversion of propane is much higher (97% at 600°C) at high temperature, and selectivities to C1 and C2 increase sharply to 22% and 15% respectively at 600°C. Figure 5.11 shows the reactivity of 28V-Mg-O(2%K) that are similar to 28V-Mg-O(3%K), but this selectivity is lower at total reaction temperature and the increasing of conversion is faster (97% at 550°C) and also to selectivities to C1, C2. The result of catalytic test of 28V-Mg-O(1%K) is shown in Figure 5.12. This figure illustrates that the selectivity to propene decreases with increasing temperature which is similar to the catalytic behavior of simple 28V-Mg-O but propane conversion is still higher at high temperature (79% at 600°C), although propene selectivity slightly decreases. However, it is lower than that of the higher content of K doping catalyst. Moreover the selectivities to C1, C2 is also lower.

From these results, it can be seen that little alkali enhance the activity become higher that lead to the higher yield at the end of temperature. But the selectivity to propene is slightly less. While the selectivity to C1 and C2 increase remarkably. In higher alkali content, nearly 100% conversion is obtained, while the selectivity to propene is less than 20%. But the selectivity to C1 and C2 are more than 20%. This increment of C1, C2 formations, it may be attributed to a change in nature of the oxidation state of the catalyst.

It can be concluded that high content of alkali doping reduce the efficiency of the catalyst. But the presence of a little amount of alkali may enhance the efficiency of the catalyst by increasing the activity at high temperature.

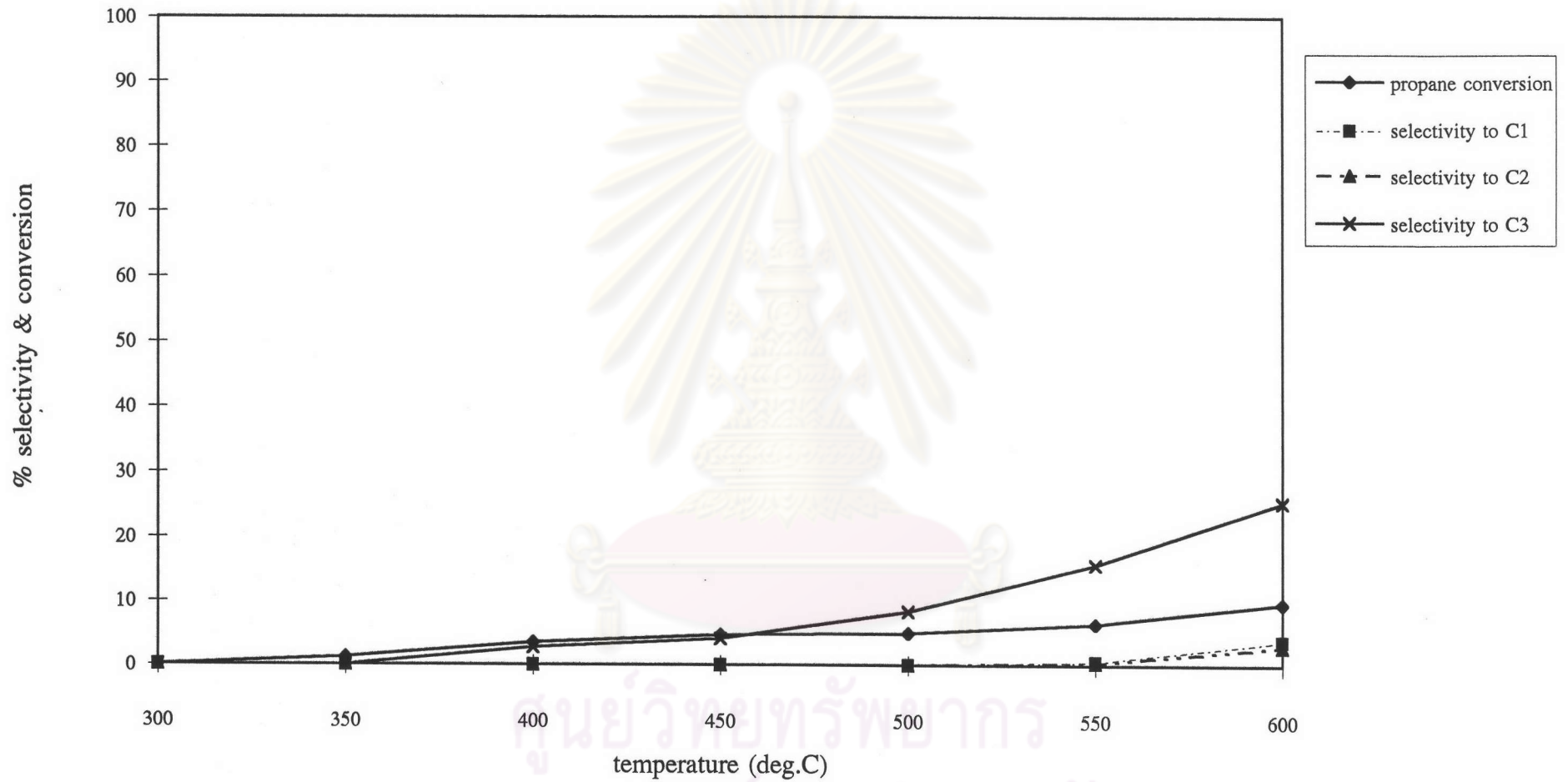


Figure 5.1 Effect of temperature on propane conversion and selectivities to C1-C3

Catalyst : blank run Condition : HC:O₂:Ar = 4:8:88

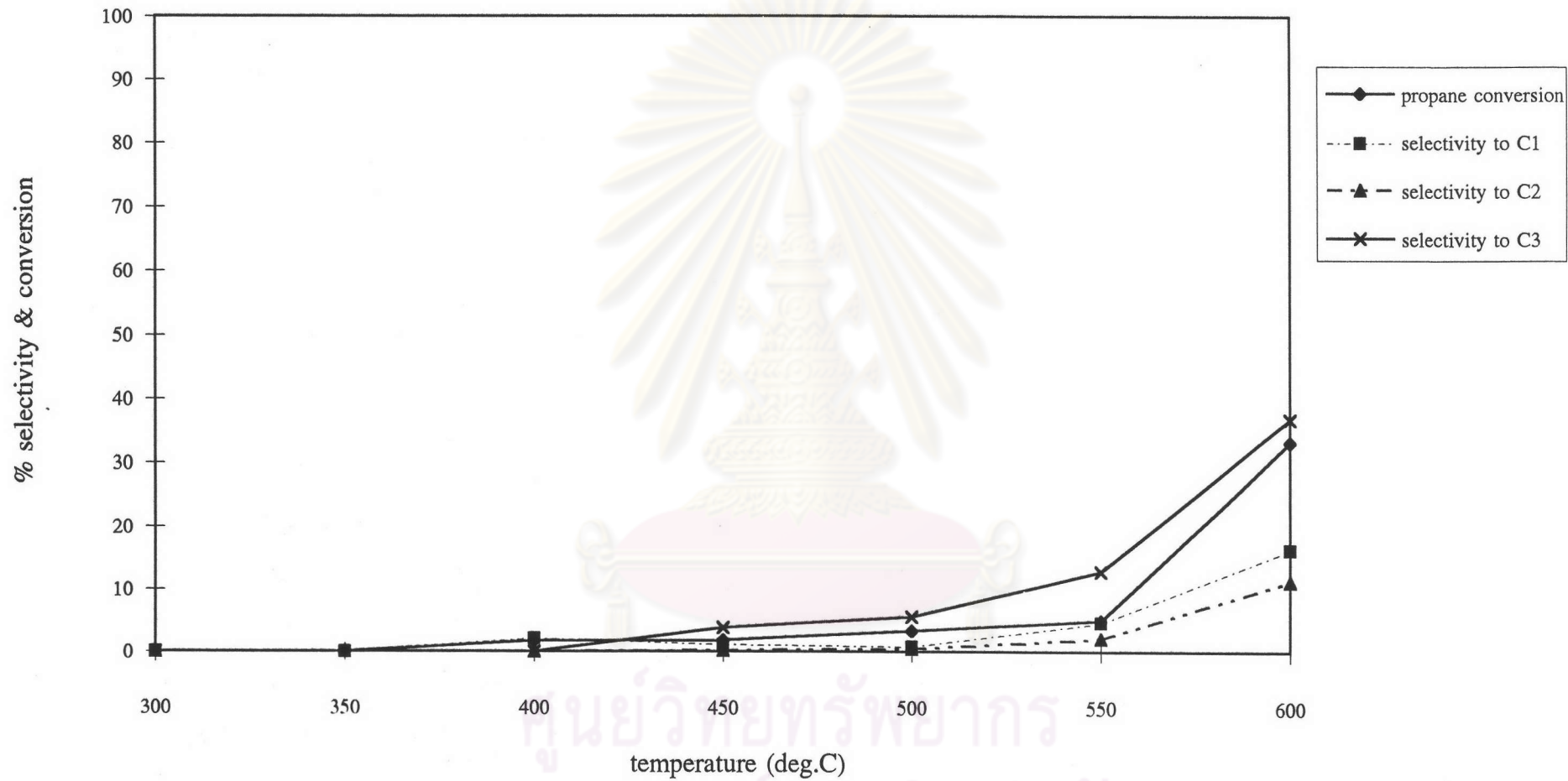


Figure 5.2 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : MgO Condition : HC:O₂:Ar = 4:8:88

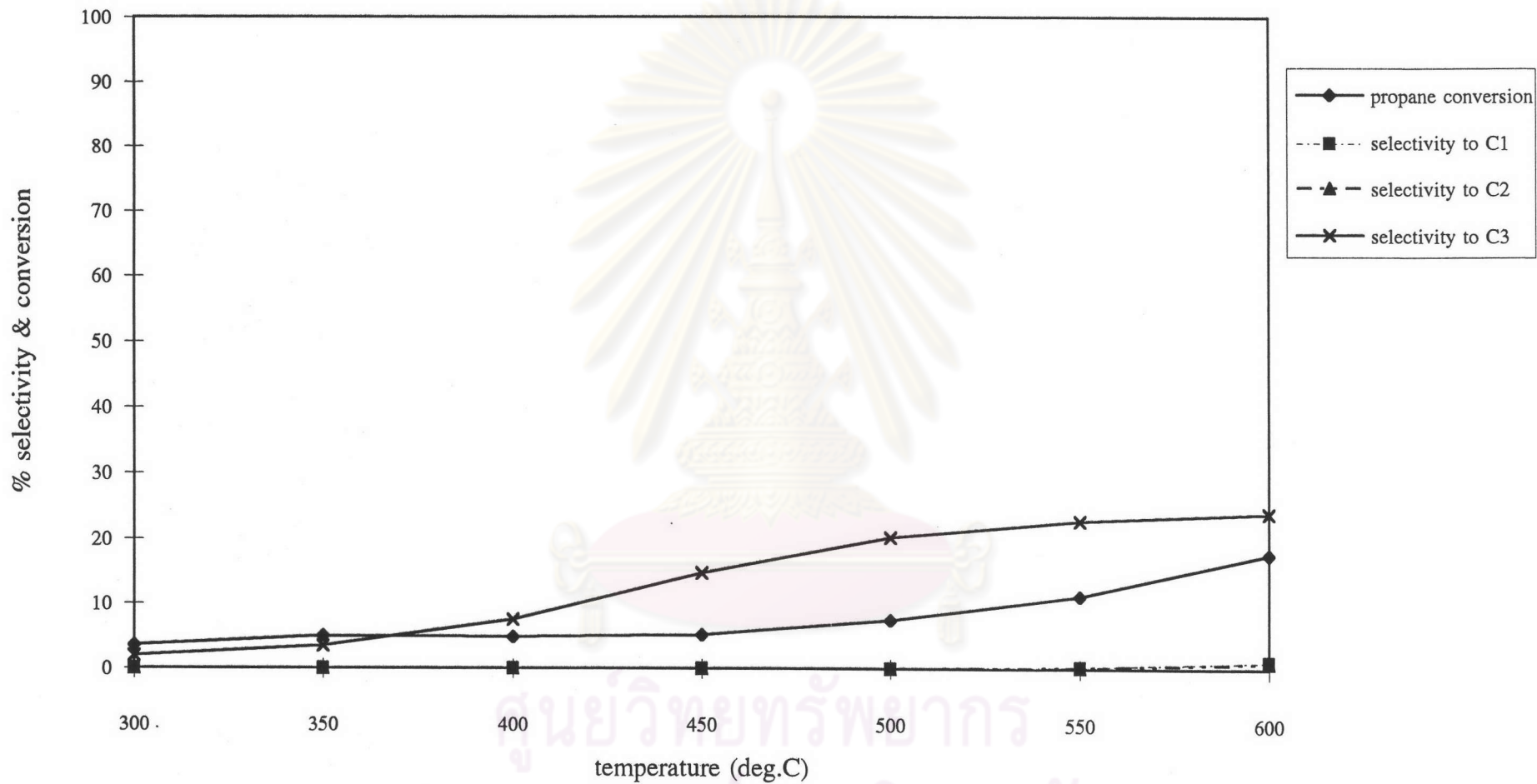


Figure 5.3 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : vanadium oxide Condition : HC:O₂:Ar = 4:8:88

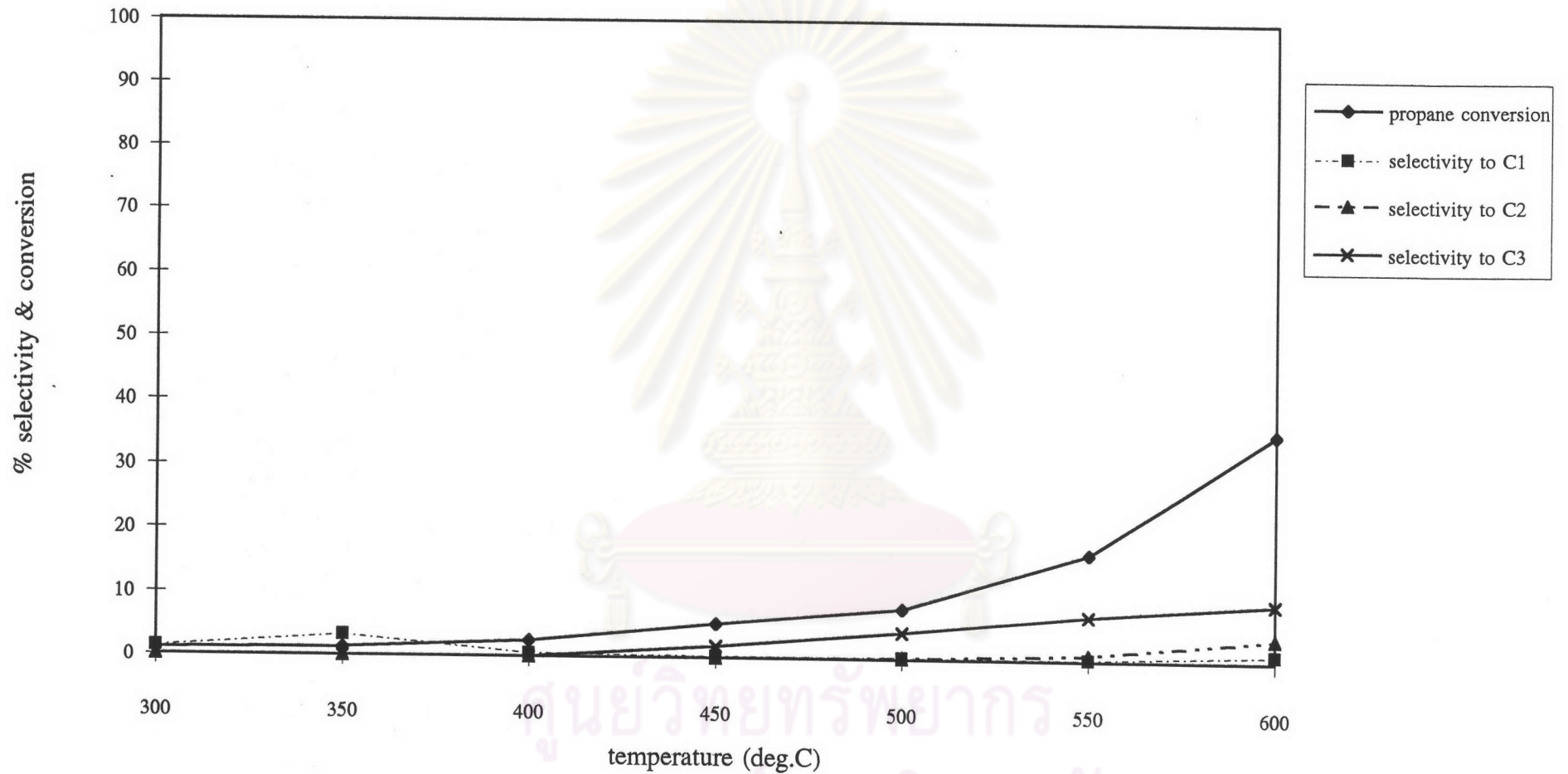


Figure 5.4 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : 4V-Mg-O Condition : HC:O₂:Ar = 4:8:88

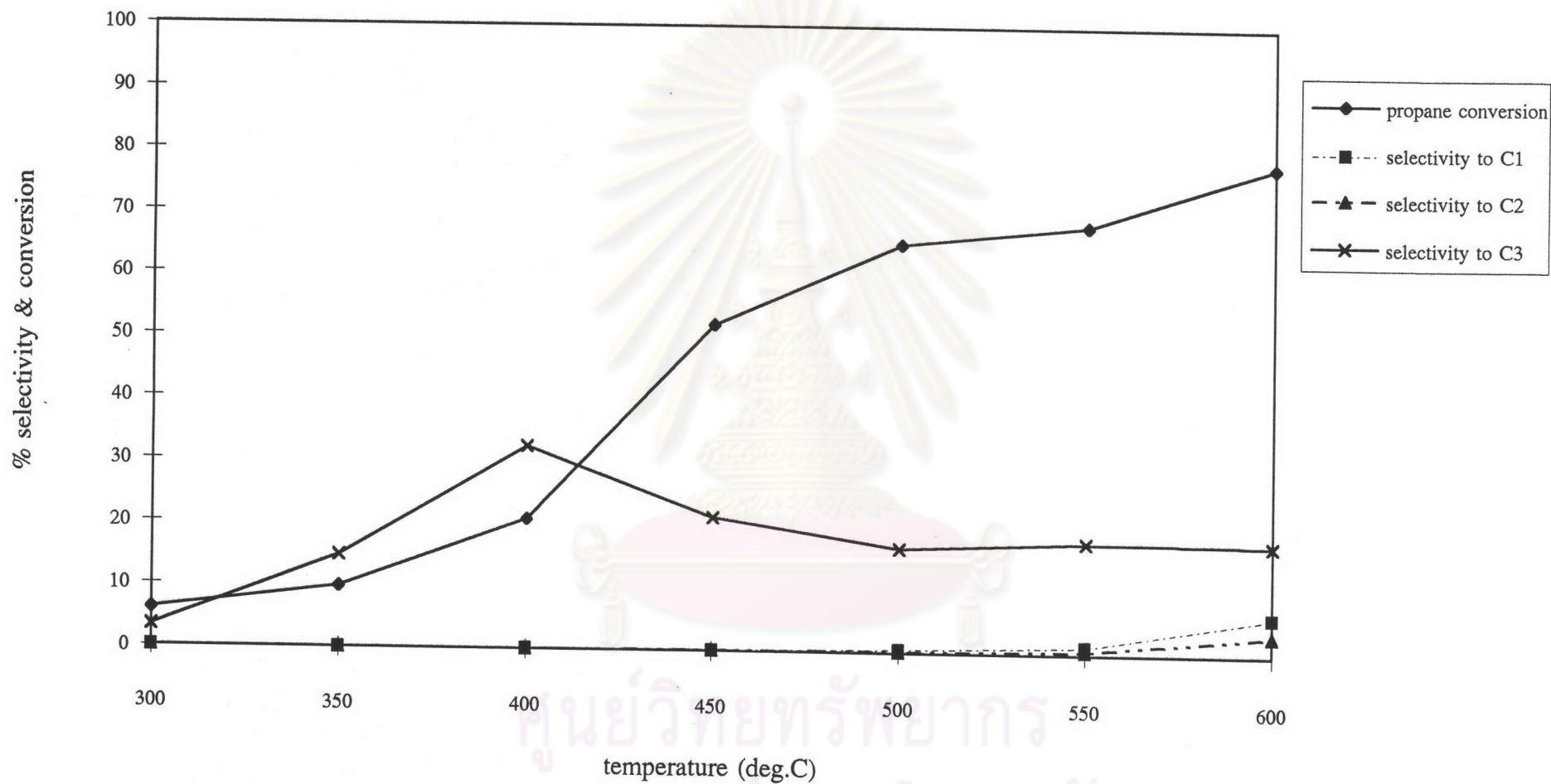


Figure 5.5 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : 21V-Mg-O Condition : HC:O₂:Ar = 4:8:88

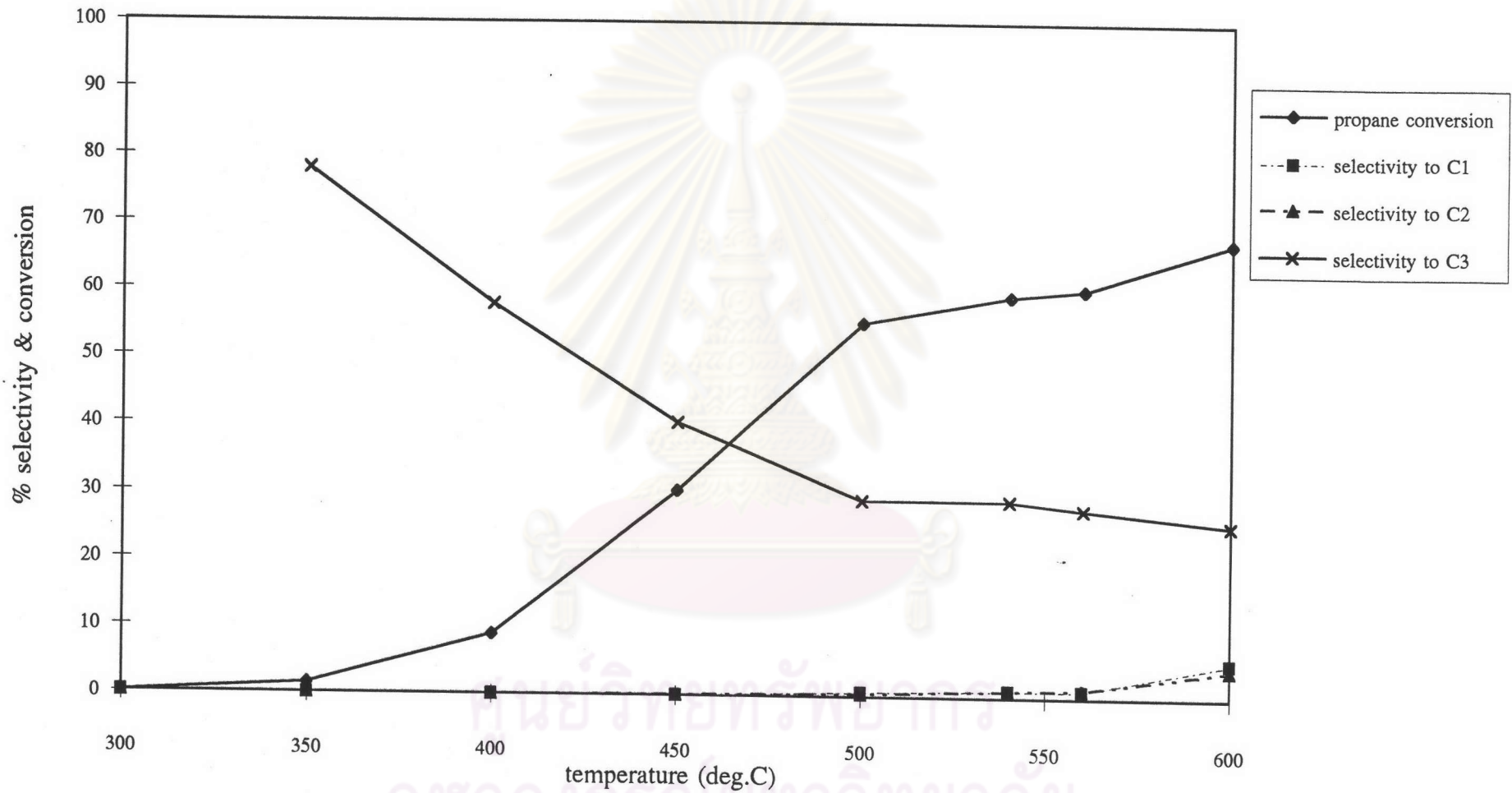


Figure 5.6 Effect of temperature on propane conversion and selectivities to C1-C3

Catalyst: 28V-Mg-O Condition: HC:O₂:Ar = 4:8:88

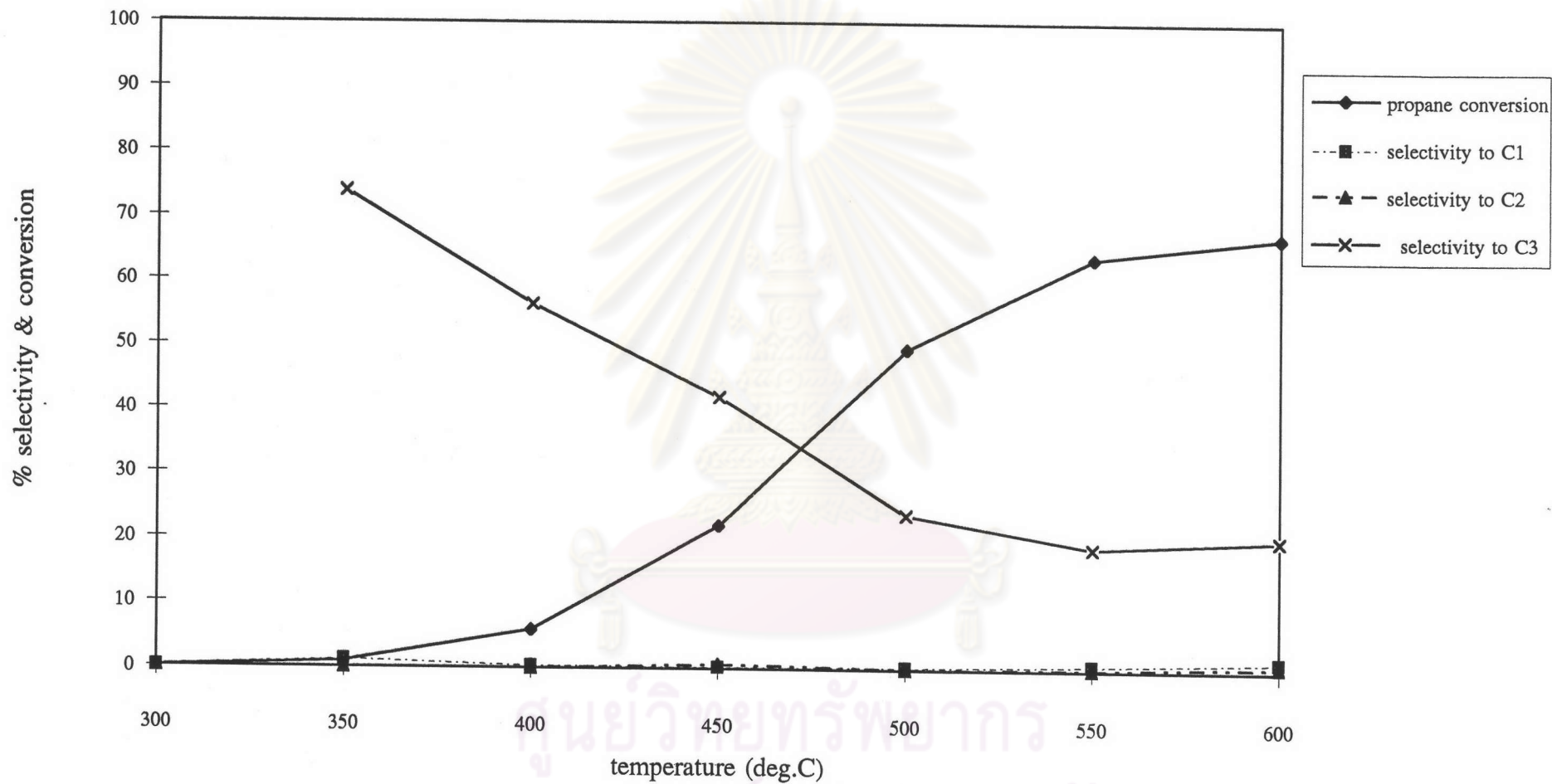


Figure 5.7 Effect of temperature on propane conversion and selectivities to C1-C3

Catalyst : 28V-Mg-O Condition : HC:O₂:Ar = 4:8:88 (repeat run)

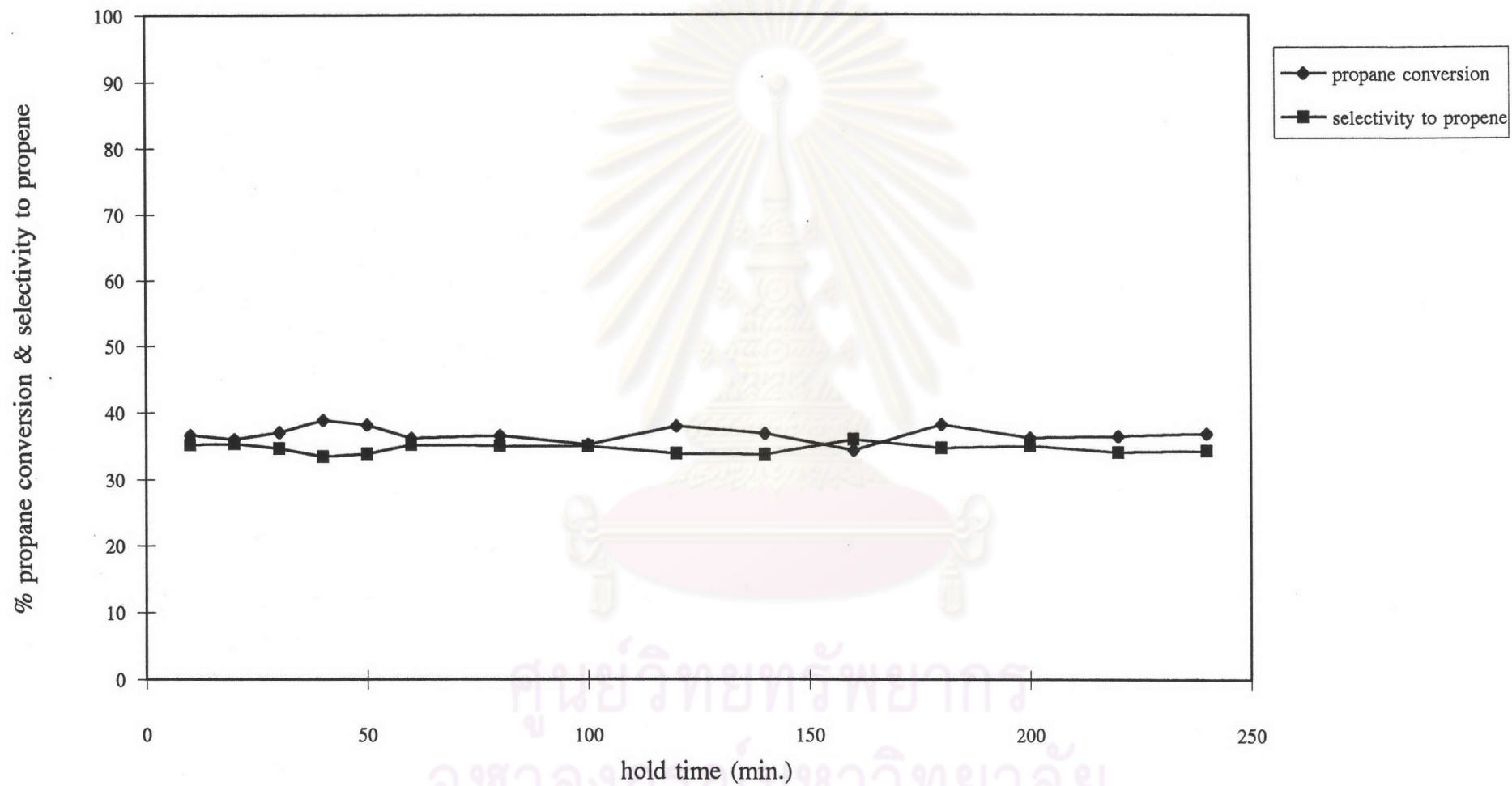


Figure 5.8 Stability of propane conversion and selectivity to propene on V-Mg-O catalyst for 4 hours at 550°C.

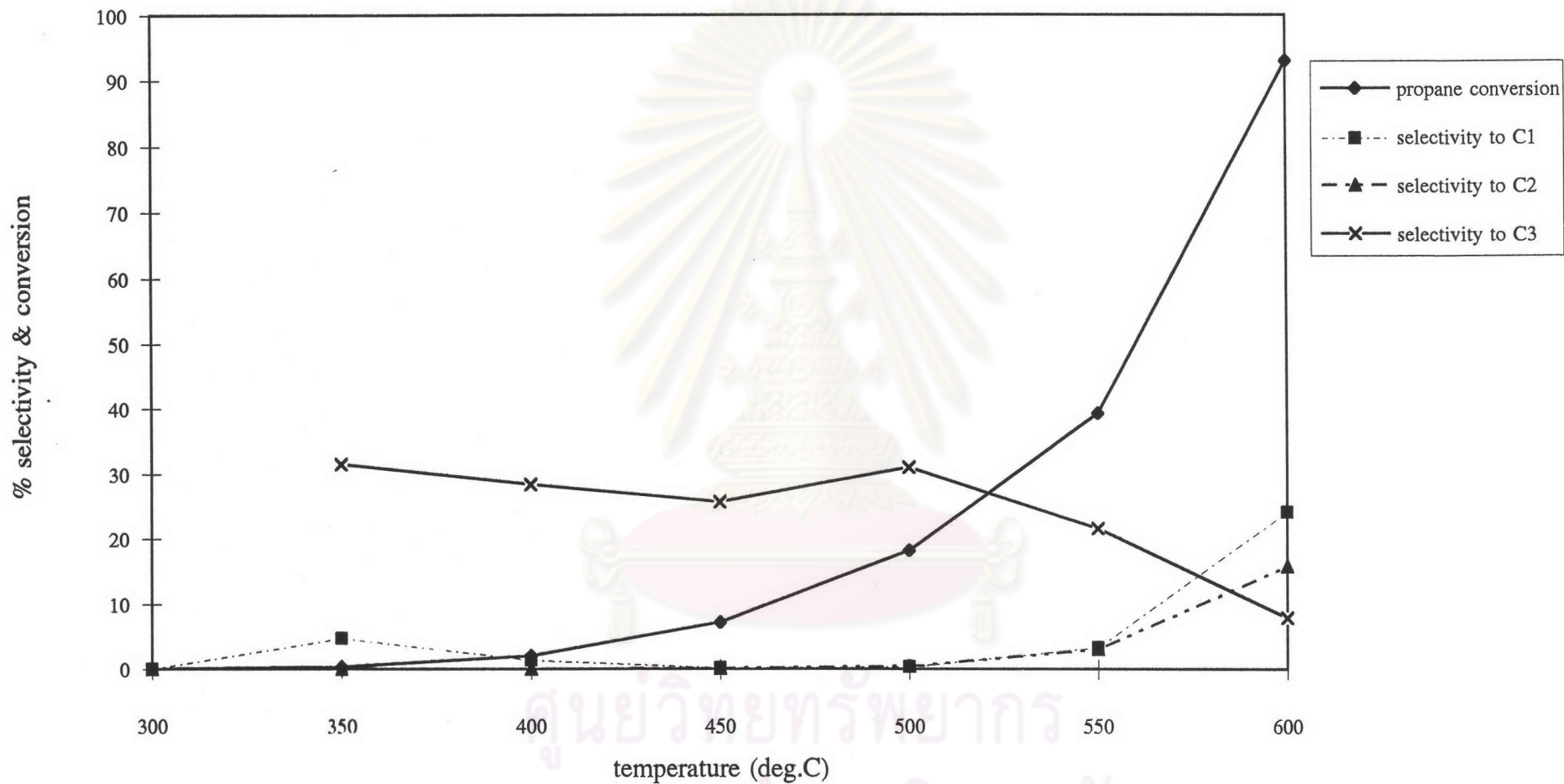


Figure 5.9 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : 28V-Mg-O(10%Na) Condition : HC:O₂:Ar = 4:8:88

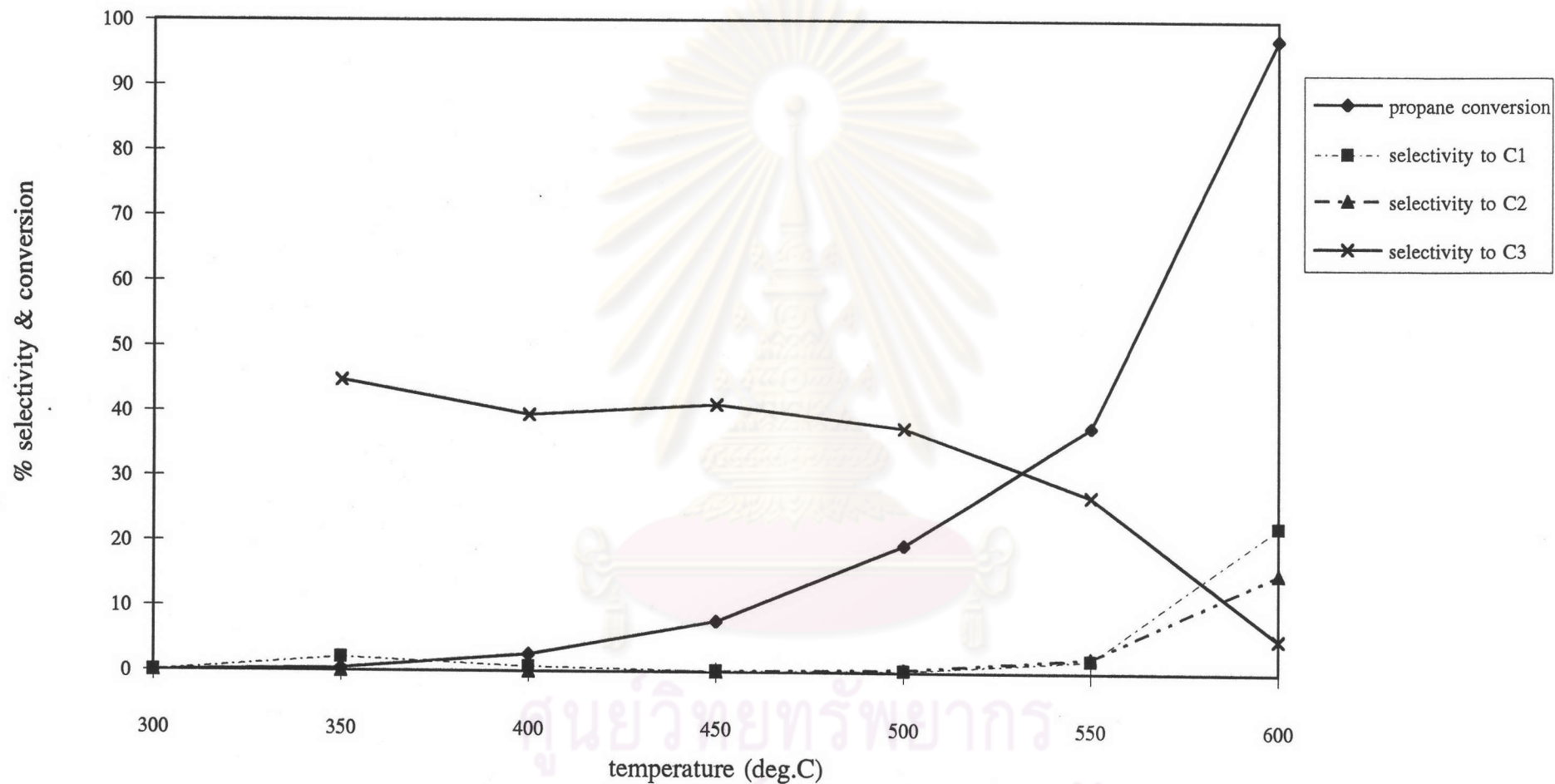


Figure 5.10 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : 28V-Mg-O(10%K) Condition : HC:O₂:Ar = 4:8:88

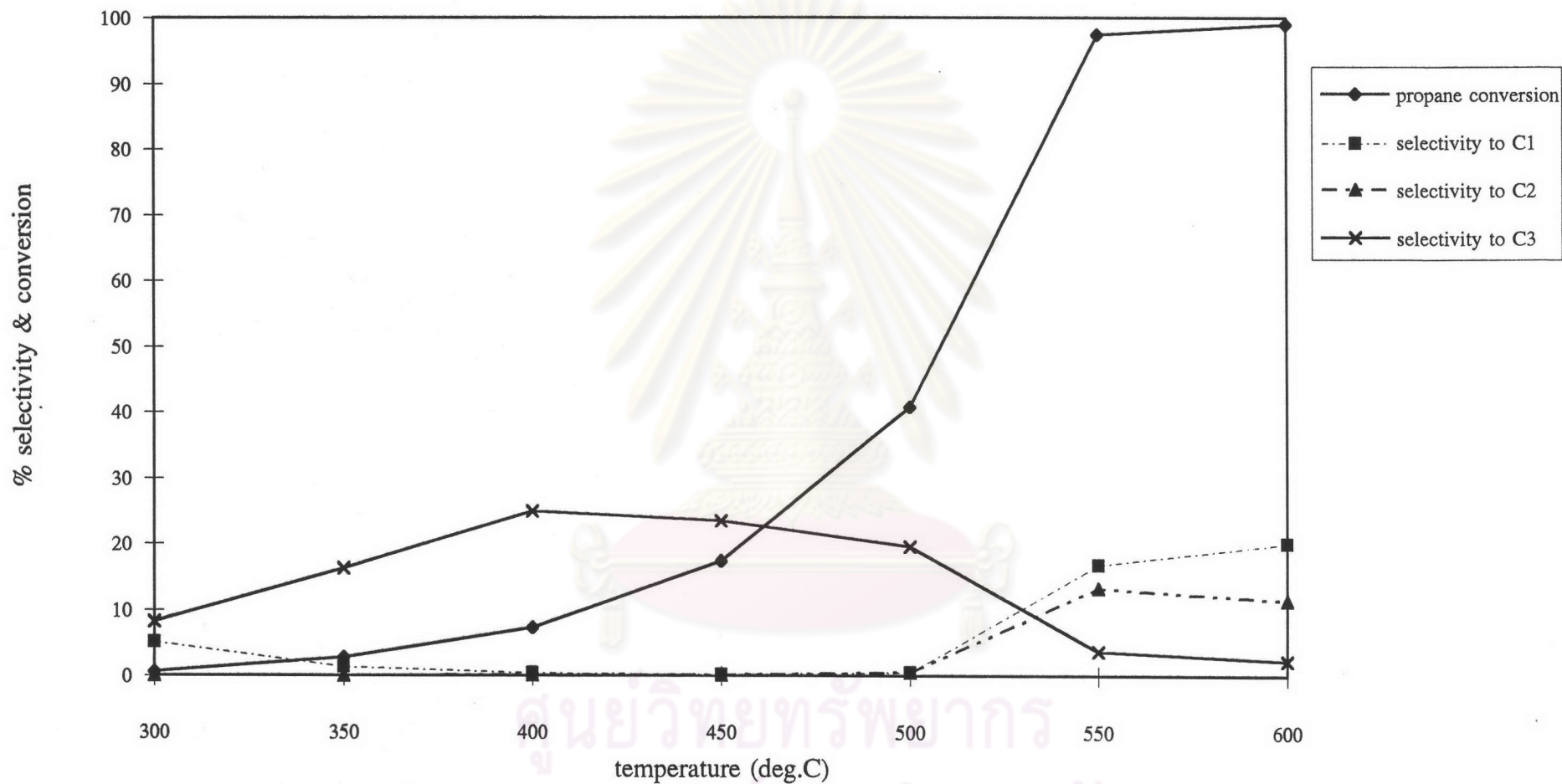


Figure 5.11 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : 28V-Mg-O(5%K) Condition : HC:O₂:Ar = 4:8:88

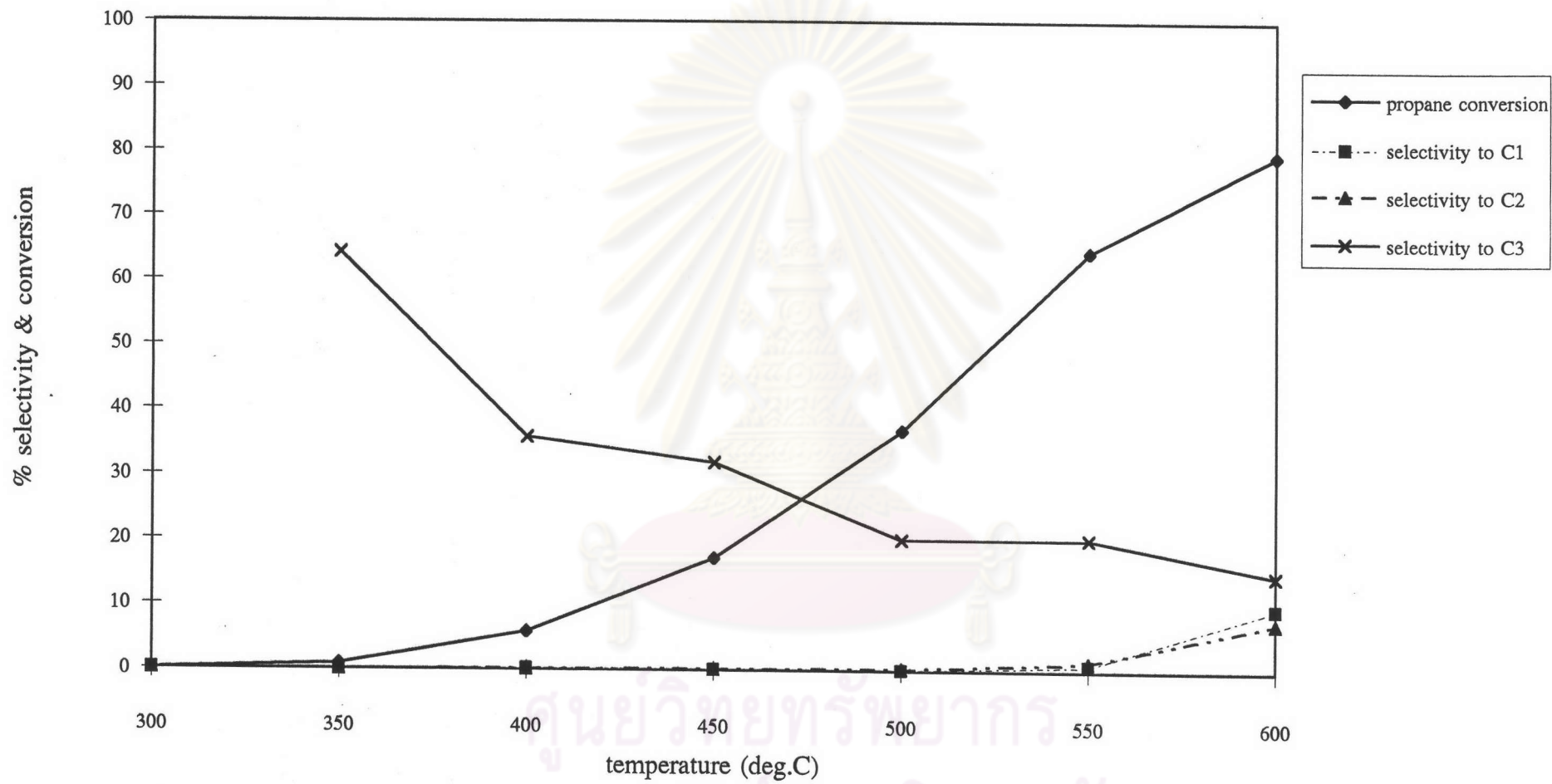


Figure 5.12 Effect of temperature on propane conversion and selectivities to C1-C3.

Catalyst : 28V-Mg-O(2%K) Condition : HC:O₂:Ar = 4:8:88

5.3 Thermogravimetric and Thermal Analysis

5.3.1 Thermogravimetric Analysis (TGA)

The weight of catalyst which lose during the heating can be measured by TGA technique, described in chapter IV. The resulted thermograms were shown in Figures 5.13 to 5.17. Each thermogram shown consists of three curves: a) temperature curve with scale on the right indicating the temperature range of the experiment, b) weight curve with scale on the left indicating the catalyst weight during the experiment and c) differentiate weight (dtg) curve with scale on the left illustrating the changing of slope of the weight curve.

TGA results of MgO are shown in Figure 5.13. Figure 5.13A is obtained from a fresh MgO sample. The figure shows that the catalyst slowly lose its weight up to a temperature around 280°C , before sharply dropped, resulting in a dtg peak around $280\text{--}405^{\circ}\text{C}$. About 15.7% of catalyst weight was lost during this drop. But when the experiment was repeated again for investigating the effect of adsorption under the same conditions using the old sample without removing it from the furnace, this sharp drop disappeared as shown in Figure 5.13B.

Figure 5.14 shows two TGA results obtained from two consecutive runs of 4V-Mg-O catalyst. For a fresh 4V-Mg-O sample (Figure 5.14A), two weight loss steps were observed. The first weight loss occurred around $50\text{--}200^{\circ}\text{C}$ (4.7 wt%) and the second occurred around $200\text{--}370^{\circ}\text{C}$ (4.4 wt%), resulting in two low and broad dtg peaks. But in the second run shown in Figure 5.14B, only a small weight loss was observed which is similar to the TGA results of MgO. The weight gain when the catalyst cooled down was also observed.

Figure 5.15 shows two TGA results obtained from two consecutive runs of 21V-Mg-O. The results obtained were similar to that of 4V-Mg-O. For a fresh 21 V-Mg-O sample, two weight loss steps were observed. The first weight loss also occurred around 50-200 °C (3.6 wt%) and the second also occurred around 200-370 °C (4.3 wt%), resulting in two low and broad dtg peaks, but in this case the peaks were lower and broader than that of 4V-Mg-O. The noisy signal in the last part of dtg curve in Figure 5.15A was attributed to the instability of power supply system, and can be disregarded because this data were at the cooled-down temperature. In the second run, a slow weight loss was observed which was similar to the TGA results of 4V-Mg-O. The weight gain when the catalyst cooled down was also observed.

TGA results obtained from 28V-Mg-O also showed similar phenomenon. Figure 5.16A is the result of a fresh sample. Two dtg peaks appeared at 50-200 °C (3.7 wt%) and 200-370 °C (2.4 wt%) indicating two weight loss steps which were similar to the results of 4V-Mg-O and 21V-Mg-O. The two peaks were much lower and broader than that of 4V-Mg-O and 21V-Mg-O (please notice that the dtg scale in Figure 5.16 is two times larger than those used in Figures 5.14, 5.15 and five times larger than that used in Figure 5.13). Figure 5.16B shows the TGA result of heating again under the same conditions using the old sample without removing it from the furnace. No dtg peak was observed in the second run. Only a slow weight decrease could be noticed.

A sample of alkali doped catalyst, 28V-Mg-O(3%K) was also analysed using TGA technique. TGA results obtained from two consecutive runs are shown in Figure 5.17. The results obtained were very similar to those belong to V-Mg-O catalyst.

From the results of TGA measurements, we can observe that all of V-Mg-O catalysts lose weight in the temperature range of 50-200°C and 200-370°C. It might be suggested that the weight loss in from the first peak is the release of moisture from the surface of catalyst but the latter one, which occurs at the temperature range of the beginning of the reaction from catalytic test part, might be the moisture in the bulk of catalyst structure which has a significant effect on ODH reaction. Furthermore, the highest percentage weight loss occurs in MgO and decreases in the following order $\text{MgO} > 4\text{V-Mg-O} > 21\text{V-Mg-O} > 28\text{V-Mg-O}$. From this order, it might be noted that MgO is a good moisture adsorption support.

Nevertheless, these lost species can be identified in the next result.



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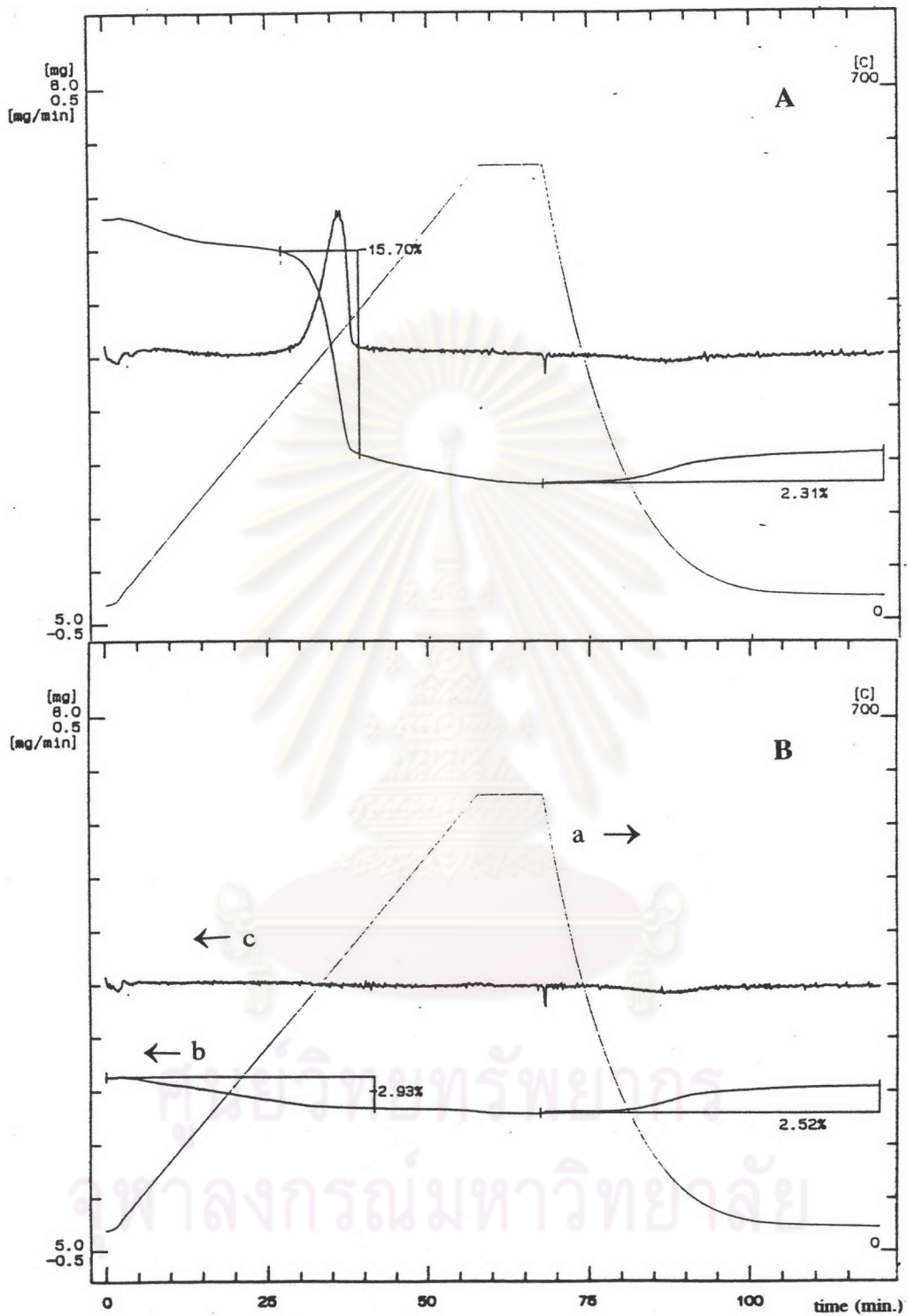


Figure 5.13 Thermogravimetric analysis of MgO: A) first run, B) second run

Measuring condition: Ar flow 30 ml/min, heating rate $10^{\circ}\text{C}/\text{min}$,

temp. range $25\text{-}600^{\circ}\text{C}$, hold time 10 min.

note: a) temperature ($^{\circ}\text{C}$) b) weight (mg) c) differentiated weight (mg/min)

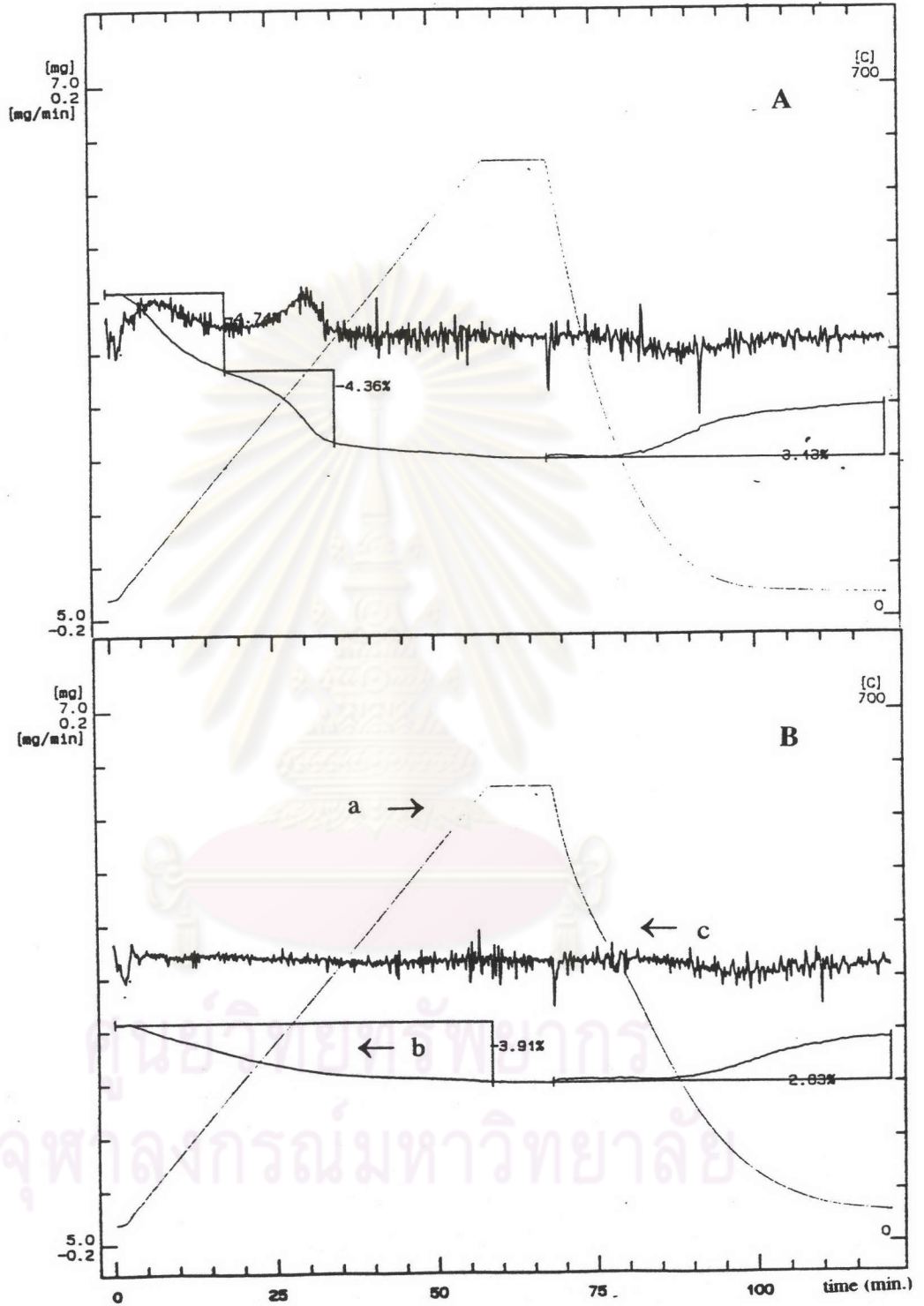


Figure 5.14 Thermogravimetric analysis of 4V-Mg-O: A) first run, B) second run

Measuring condition: Ar flow 30 ml/min, heating rate $10^{\circ}\text{C}/\text{min}$,

temp. range $25\text{--}600^{\circ}\text{C}$, hold time 10 min.

note: a) temperature ($^{\circ}\text{C}$) b) weight (mg) c) differentiated weight (mg/min)

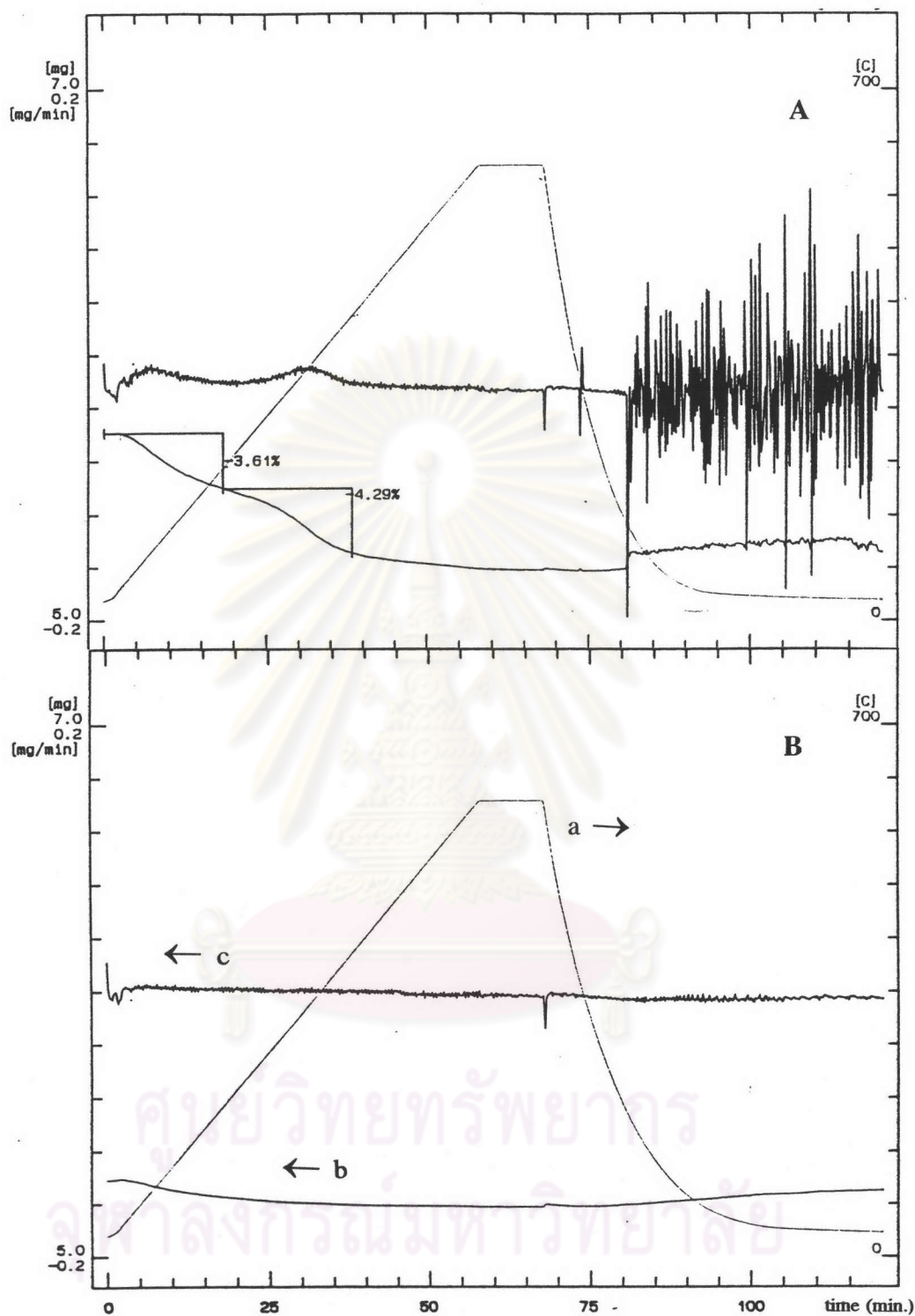


Figure 5.15 Thermogravimetric analysis 21V-Mg-O: A) first run, B) second run

Measuring condition: Ar flow 30 ml/min, heating rate $10^{\circ}\text{C}/\text{min}$,

temp. range $25\text{-}600^{\circ}\text{C}$, hold time 10 min.

note: a) temperature ($^{\circ}\text{C}$) b) weight (mg) c) differentiated weight (mg/min)

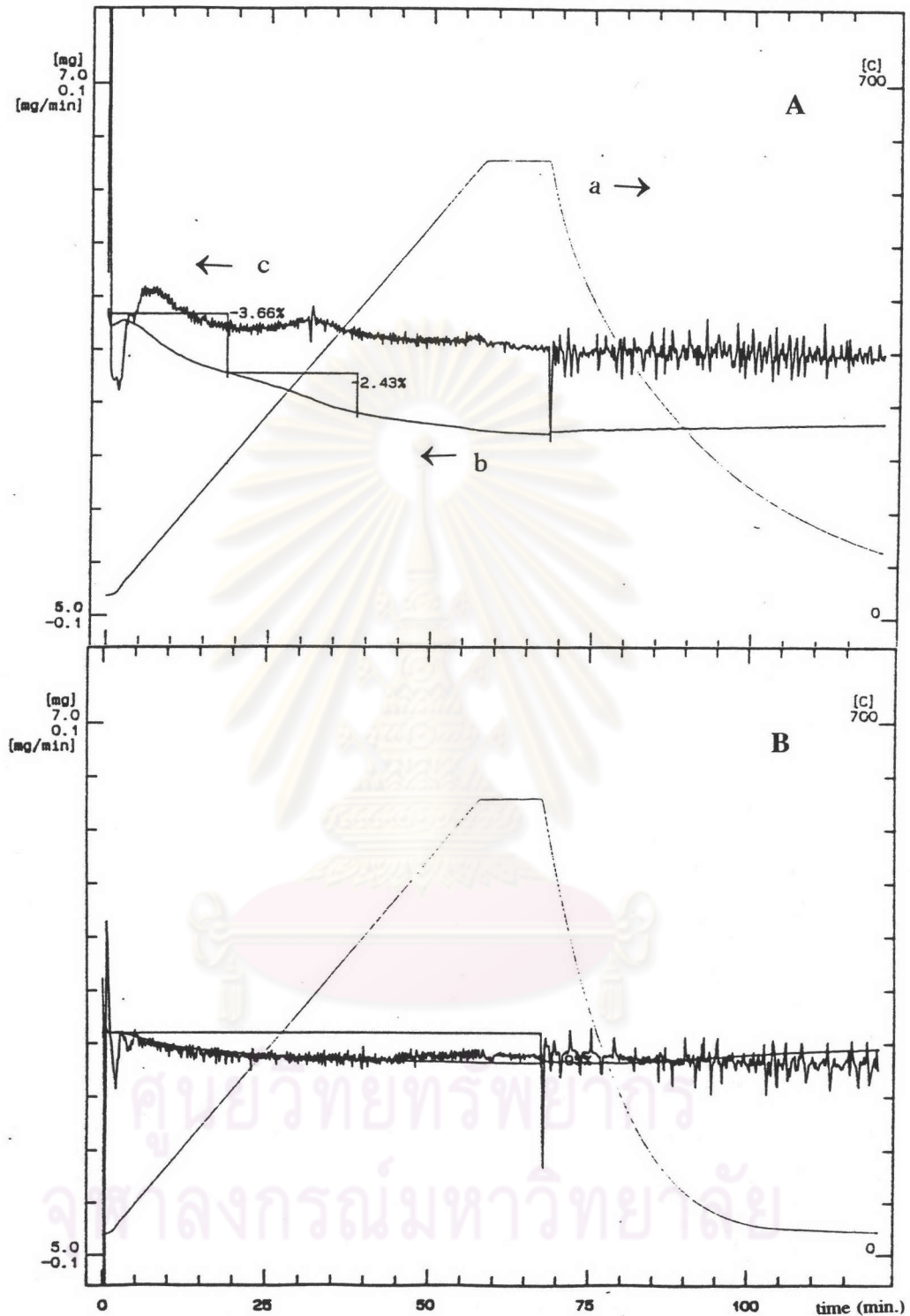


Figure 5.16 Thermogravimetric analysis of 28V-Mg-O: A) first run, B) second run

Measuring condition: Ar flow 30 ml/min, heating rate $10^{\circ}\text{C}/\text{min}$,

temp. range $25\text{-}600^{\circ}\text{C}$, hold time 10 min.

note: a) temperature ($^{\circ}\text{C}$) b) weight (mg) c) differentiated weight (mg/min)

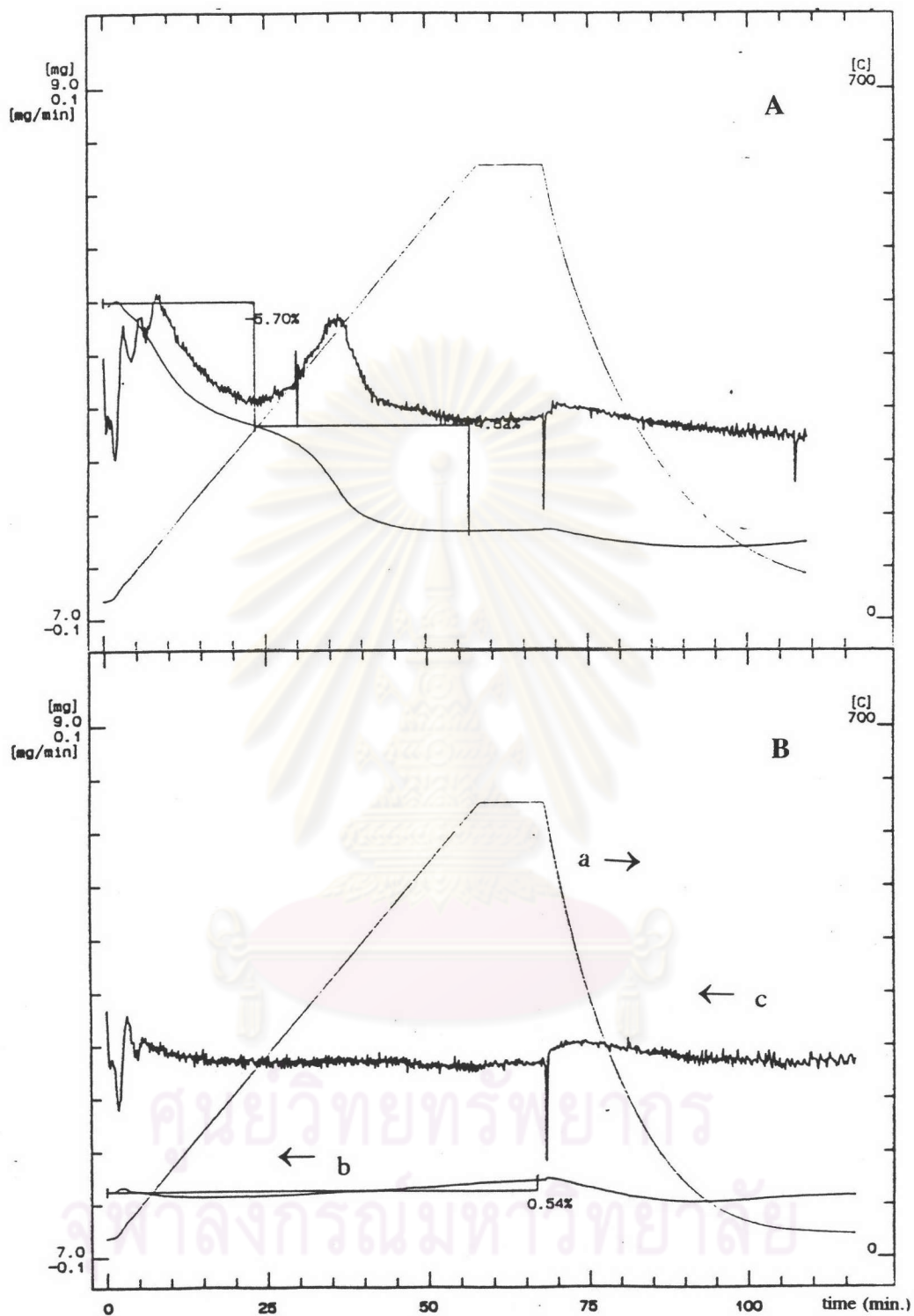


Figure 5.17 Thermogravimetric analysis of 28V-Mg-O(3%K): A) first run,
 B) second run. Measuring condition: Ar flow 30 ml/min, heating rate $10^{\circ}\text{C}/\text{min}$,
 temp. range $25\text{-}600^{\circ}\text{C}$, hold time 10 min.

note: a) temperature ($^{\circ}\text{C}$) b) weight (mg) c) differentiated weight (mg/min)

5.3.2 Thermal Analysis

To identify species lost during heating in TGA, the effluent gas was analysed using GC which was described in chapter 4. Typical results obtained from MgO and 28V-Mg-O (no alkali doping) samples are shown in Figures 5.18 and 5.19 respectively. The figures show the comparison of the amount of O₂ and H₂O in the same unit but in different scales on Y axis for showing the shape of O₂ curve. It was found that H₂O was the main species lost from the catalysts accompanied with a small amount of O₂. O₂ loss becomes significant with H₂O loss in the temperature range 200-400 °C which is the second dtg peak in the case of V-Mg-O catalysts.

The presence of surface moisture on supported vanadium oxide has been proposed recently [25], but this presence of surface moisture was not determined in the case of V-Mg-O system.

It is observed that for each catalyst the temperature which the catalyst become active during the ODH reaction and the temperature at which O₂ and H₂O loss began are in the same temperature range. This observation indicates that there should be some relationship between activity and the loss of H₂O and O₂ from the catalyst. It is known that the surface of supported vanadium catalysts are usually covered by a layer of adsorbed water [25]. This water layer inhibits the adsorption of reactant on the catalyst surface, thus makes the catalyst inactive. Heating the catalyst up to a specific temperature can remove this water layer resulting in the exposure of active sites.

It is also known that in the ODH reaction on oxide catalysts, hydrocarbon will extract O₂ from the catalyst surface at low temperature [2]. HC conversion will depend on the ease of catalyst surface reduction. Heating the catalyst enhances the releasing of O₂ from the catalyst surface and results in the initiation of the ODH reaction. High selectivity at initial state may be caused by the reaction between

HC and O₂ from the catalyst surface. At high temperature adsorbed oxygen which is adsorbed from the gas phase may significantly involve in the oxidation. It was demonstrated that this adsorbed O₂ species preferred non-selective oxidation [29,64].



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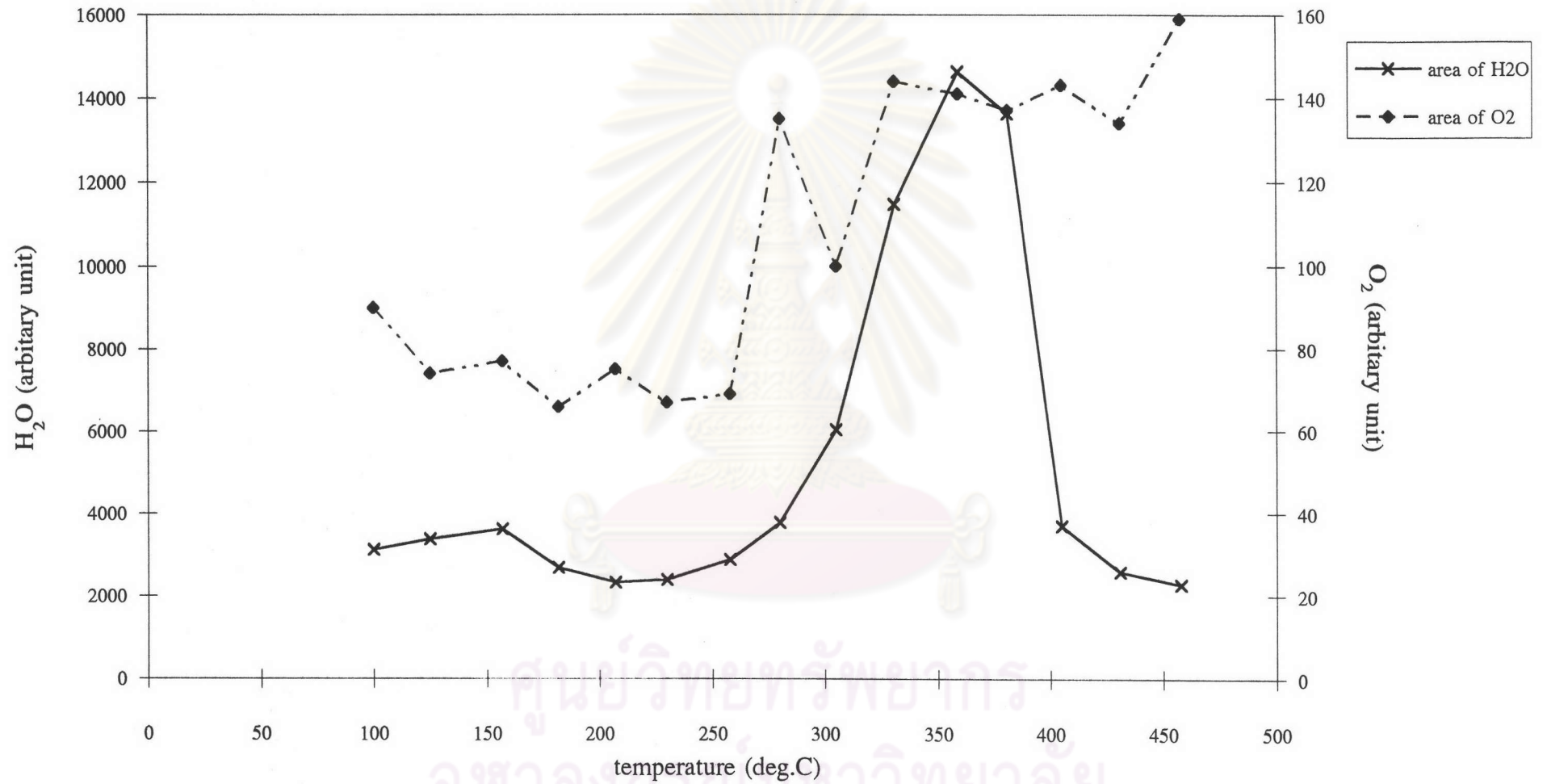


Figure 5.18 GC chromatogram of effluent gas from TGA of MgO

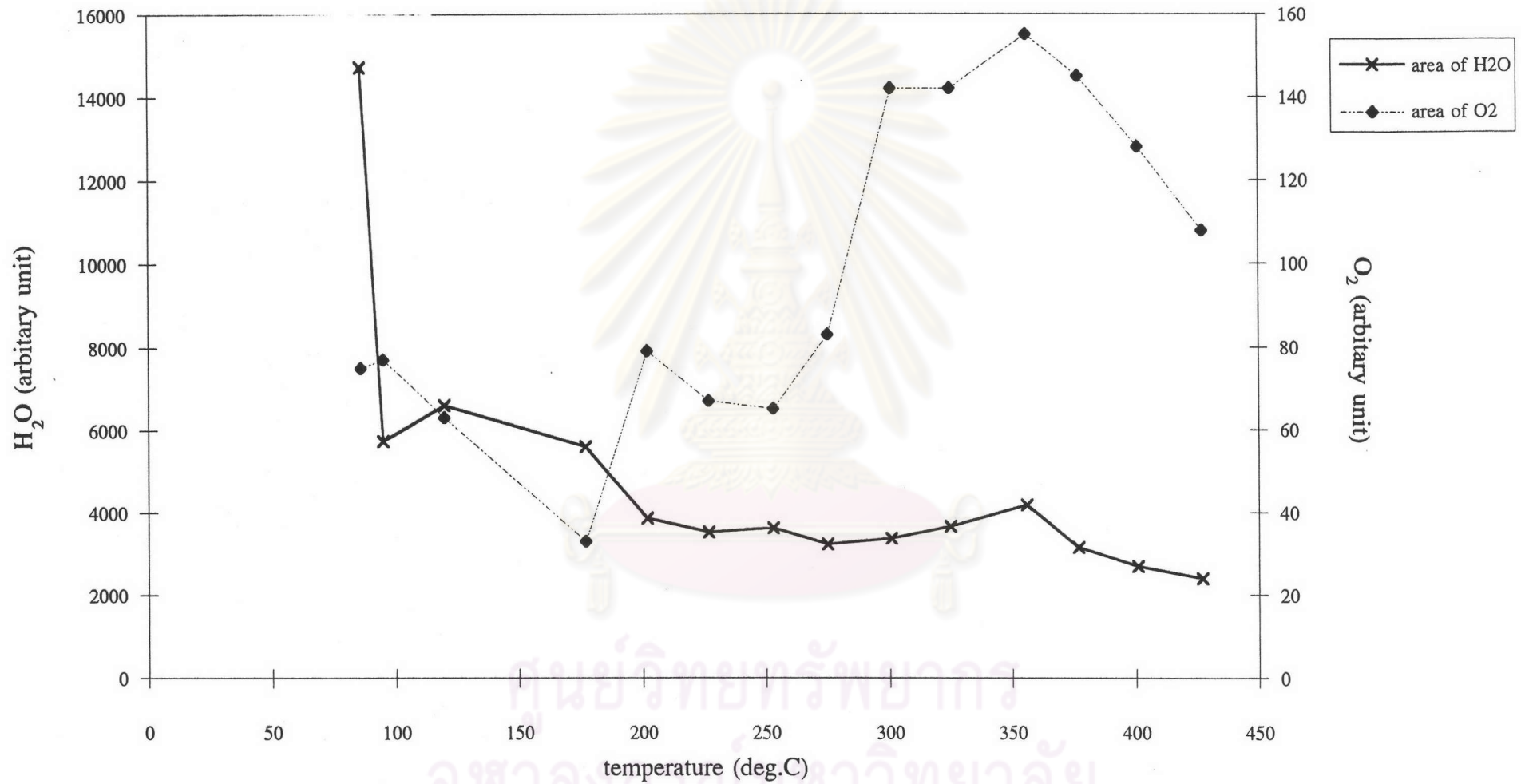


Figure 5.19 GC chromatogram of effluent gas from TGA of 28V-Mg-O

5.4 Catalyst Characterization

5.4.1 X-ray Diffraction Study

Table 5.3 X-ray diffraction lines from catalysts and their assignments

<i>d</i> spacing (Å) (relative intensity)							
V ₂ O ₅	MgO	3V-Mg-O	19V-Mg-O	24V-Mg-O	V-Mg-O(Na)	V-Mg-O(K)	Assignment [81]
	1.489	1.495	1.491	1.495	1.491	1.489	MgO
	2.111	2.116	2.111	2.111	2.115	2.116	MgO
	2.434	2.440	2.453	2.490	2.434	2.434	MgO
2.882							V ₂ O ₅
3.411							V ₂ O ₅
4.381							V ₂ O ₅

Results of X-ray diffraction of catalysts used in this research are presented in Table 5.3 and Figures 5.20-5.23. It should be noted here that any structures which do not form multilayer or large enough crystal cannot be detected by this technique. Figure 5.20 illustrates the XRD spectra of V₂O₅. The most evident three lines of V₂O₅ spectra have the 2θ value of 20.5, 26.5, and 31.8. MgO, shown in Figure 5.21, consists XRD spectra having the 2θ value of 37, 43, and 62.8. Figure 5.22 shows the evident spectra of V-Mg-O catalysts that have the 2θ value of around 37, 43 and 62.8 which belong to MgO spectra. It can be seen that V₂O₅ peak is unobservable in all V-Mg-O catalysts, only MgO diffraction lines were detected, which means that no large V₂O₅ crystal formed on MgO surface. It is known that vanadium supported on MgO catalysts tends to form stable V-Mg-O compounds rather than vanadium oxides. There have been reported that V-Mg-O with vanadium content over 35%V can exhibit the diffraction line of Mg₃V₂O₈ [1].

Hence, the unobservable diffraction lines of any V-Mg-O compounds, i.e. $\text{Mg}_3\text{V}_2\text{O}_8$, MgV_2O_6 , and $\text{Mg}_2\text{V}_2\text{O}_7$, indicates that possibly only very thin layer of V-Mg-O compounds were formed on the catalyst surface.

It was suggested that V-Mg-O compounds formation depended on the amount of vanadium [25]. Therefore, the possible V-Mg-O compound formed on 4 V-Mg-O, 21V-Mg-O and 28V-Mg-O should be only $\text{Mg}_3\text{V}_2\text{O}_8$ and $\text{Mg}_2\text{V}_2\text{O}_7$ for the catalysts used in this research.

Moreover, it can be observed from Figure 5.23 that the spectra of mainly MgO line is sharper both in spent catalyst (i.e. catalyst that was passed through the ODH reaction) and in heated catalyst (i.e. catalyst that was passed through heating at 550°C in the air for 3 hours). The explanation of the broadening of fresh V-Mg-O is owing to the moisture in their structure. Furthermore, Figure 5.23 also shows no effect of heating both in only air and in reactant on the spectra of V-Mg-O.

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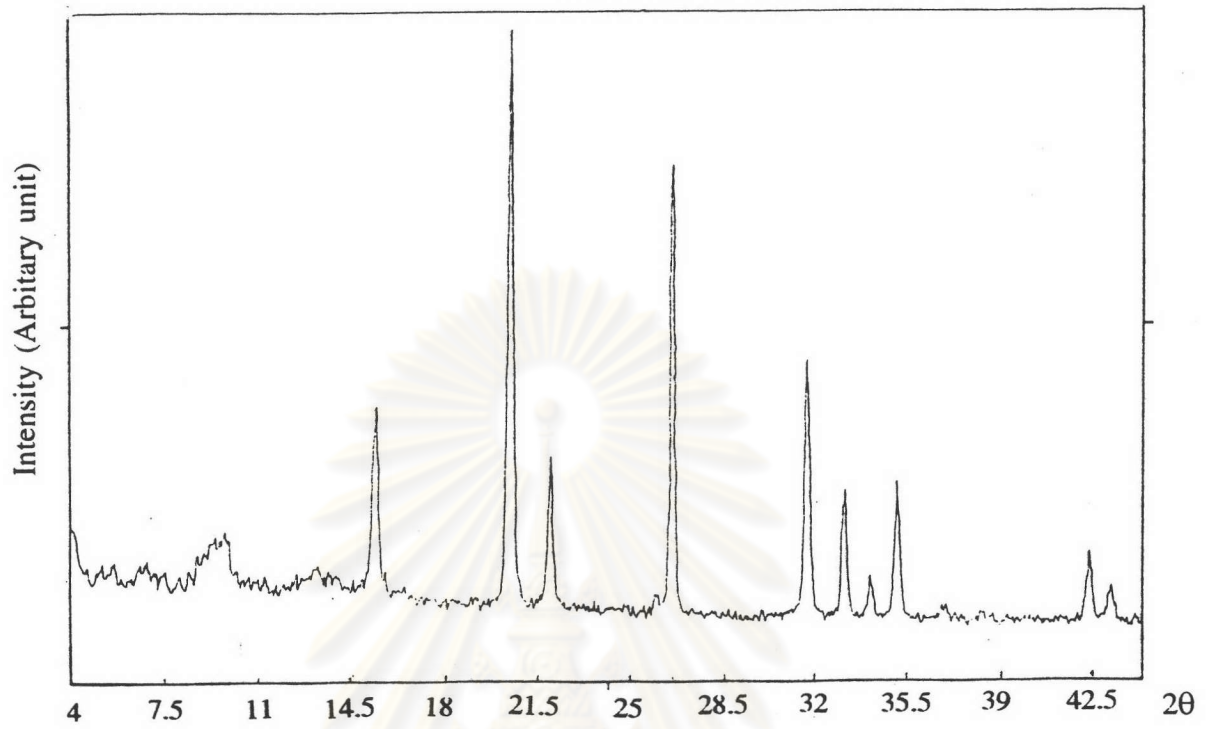


Figure 5.20 X-ray diffraction pattern of V_2O_5

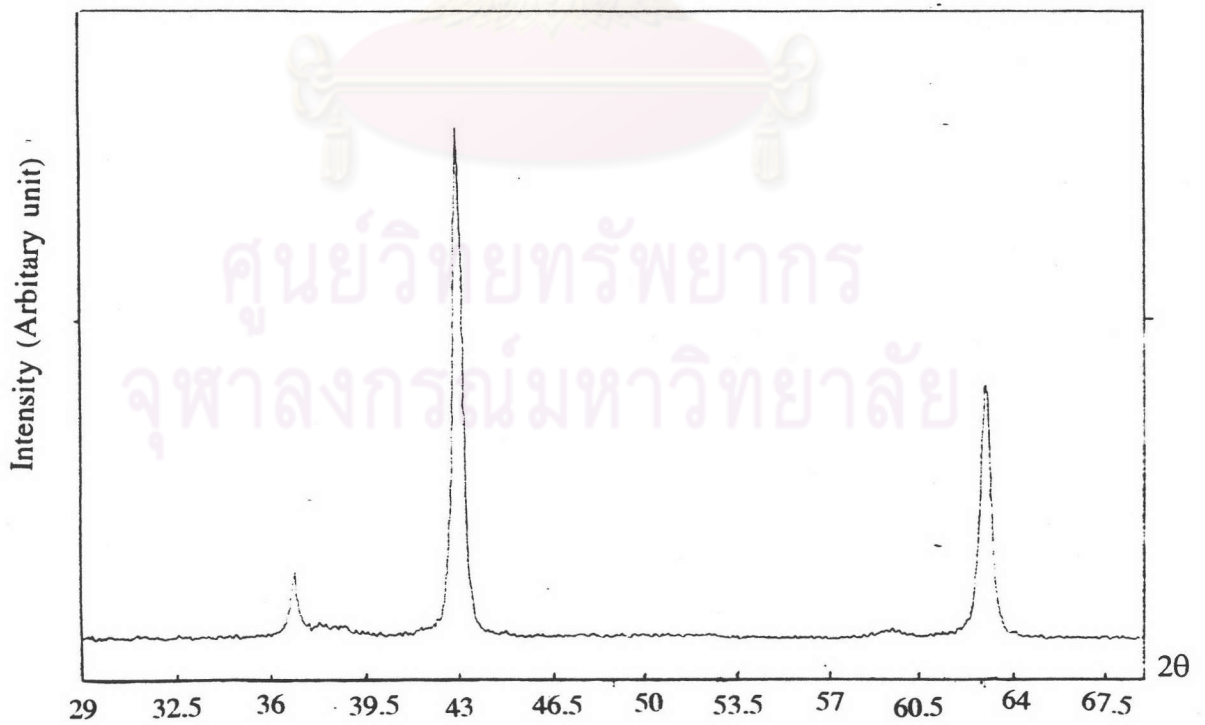


Figure 5.21 X-ray diffraction pattern of MgO

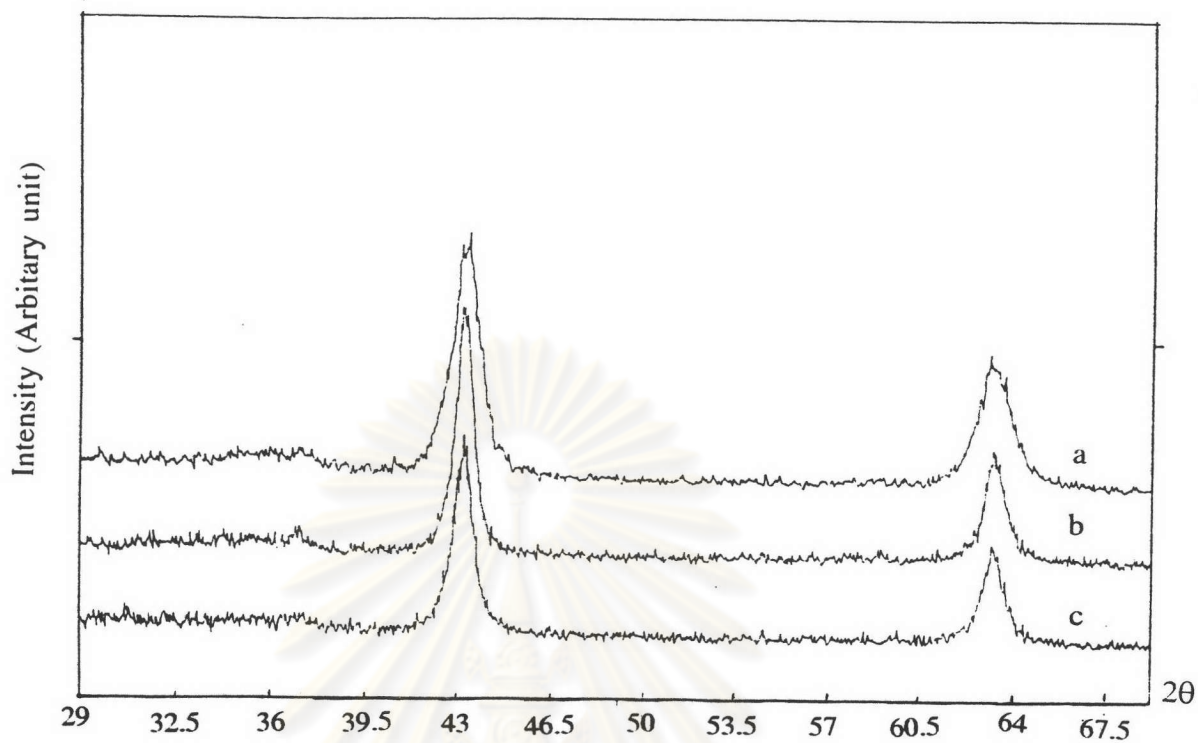


Figure 5.22 X-ray diffraction patterns of V-Mg-O catalysts: a) 28V-Mg-O, b) 21V-Mg-O, c) 4V-Mg-O

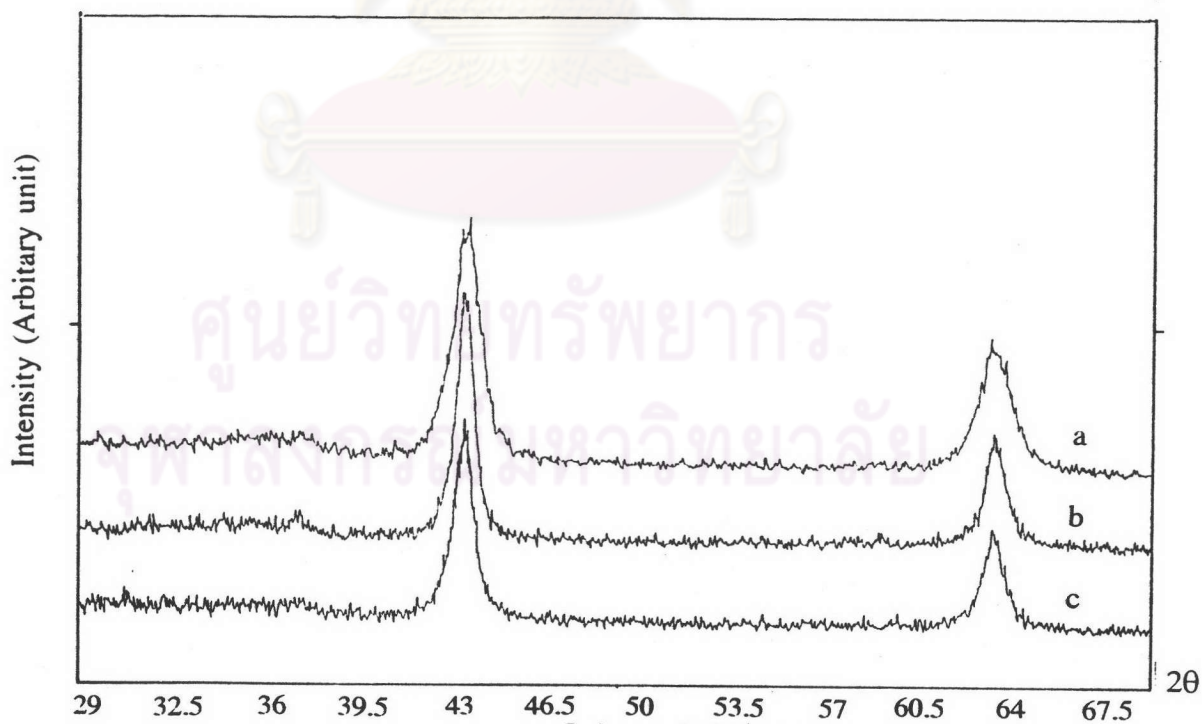


Figure 5.23 X-ray diffraction patterns of a) spent 28V-Mg-O, b) heated 28V-Mg-O, c) fresh 28V-Mg-O

5.4.2 IR Spectroscopy

The IR spectra of the catalysts used in this research are shown in Figures 5.24-5.32. The IR spectrum of V_2O_5 (Figure 5.24) shows a strong peaks at 1022, 833, 614 and 492 cm^{-1} . The weak peak appearing around 1640 cm^{-1} is the background peak coming from KBr. The peak at 1022 cm^{-1} can be assigned to the vibration of V=O [1].

IR spectrum of MgO (Figure 5.25) exhibits three weak peaks at 1459, 1123 and 868 cm^{-1} . Very strong adsorbance band appears in the region $400\text{-}800\text{ cm}^{-1}$. It seems that this region comprises of at least two strong peaks at 654.6 and 482 cm^{-1} that overlap each other.

IR spectrum of 4V-Mg-O is shown in Figure 5.26. The spectrum is similar to that of MgO. In this case, the peak at 1459 cm^{-1} becomes very strong and a well defined shoulder appears at around 630 cm^{-1} . The absorbance at 868 cm^{-1} becomes stronger. It should be noted here that the absorbance band at 1022 cm^{-1} which belongs to V=O disappears. This disappearance of V=O has been reported in several literature [1,11,16,17,24,25]. It has been suggested that V=O preferred the formation of oxygenates which were the precursors of carbon oxides.

IR spectra of 21V-Mg-O and 28V-Mg-O are shown in Figures 5.27 and 5.28 respectively. The spectra are also similar to that of 4V-Mg-O. When the vanadium content was increased from 4 to 21 wt%, the peak at 1459 cm^{-1} significantly drops while the peak at 863 cm^{-1} becomes stronger. The shoulder at 665 cm^{-1} becomes clearer. When the vanadium content was further increased to 28%, the strength of the peak at 1455 cm^{-1} further drops while the peaks at 844 and 669 cm^{-1} become stronger.

The peaks at around 860 and 660 cm^{-1} can be assigned to the vibration frequency of VO_3 and V-O-V respectively [82]. These vibrations are belong to the Mg pyrovanadate compound. The results in IR technique confirm that there is a

thin layer of Mg pyrovanadate on V-Mg-O which XRD technique can not detect. The disappearance of V=O and the appearance of VO₃ and V-O-V bonds in V-Mg-O catalyst confirm that V=O is not active and selective for this ODH reaction. VO₃ and V-O-V bonds are the most likely active and selective surface species. Moreover, the absence of V=O on V-Mg-O surface confirms that vanadium does not form as monolayer V₂O₅ like other supported vanadium oxide.

The effect of heating the catalysts sample which were heated in air at 550 °C for 3 hours is also investigated with IR spectroscopy. Their results were shown in Figure 5.29. There is no any new peak in both samples and small change in shape of spectra is only observed. There is an evidence change of lost of peak at 1120 cm⁻¹ (MgO) in both spent catalysts of 21V-Mg-O and 28V-Mg-O (as seen in Figure 5.30) which were used in the ODH reaction with propane. This is a significant observation. However, the explanation for this phenomena cannot be given at this time.

IR spectra of Na and K doped catalysts are demonstrated in Figures 5.31 and 5.32 respectively. The shape and relative strength of each peak is still similar to that of base 28V-Mg-O. The main difference is the noisy signal appeared in the regions 1400-1800 cm⁻¹ and 600-800 cm⁻¹. At this moment, this phenomenon can not be explained. Alkali seems to mainly disturb V-O-V structure without any effect on VO₃ structure. It is hypothesised that alkali may form M-O-M structure, where M may be vanadium or alkali. The loss of V-O-V structure accompanied with the loss of propene selectivity suggests that V-O-V structure is the active and selective species for the ODH of propane.

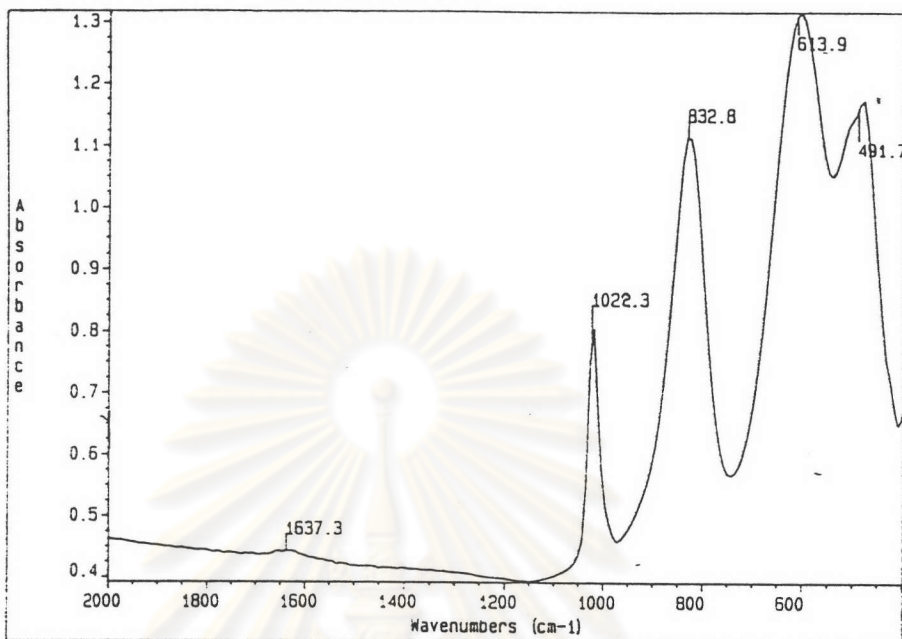


Figure 5.24 Infrared spectra of V_2O_5

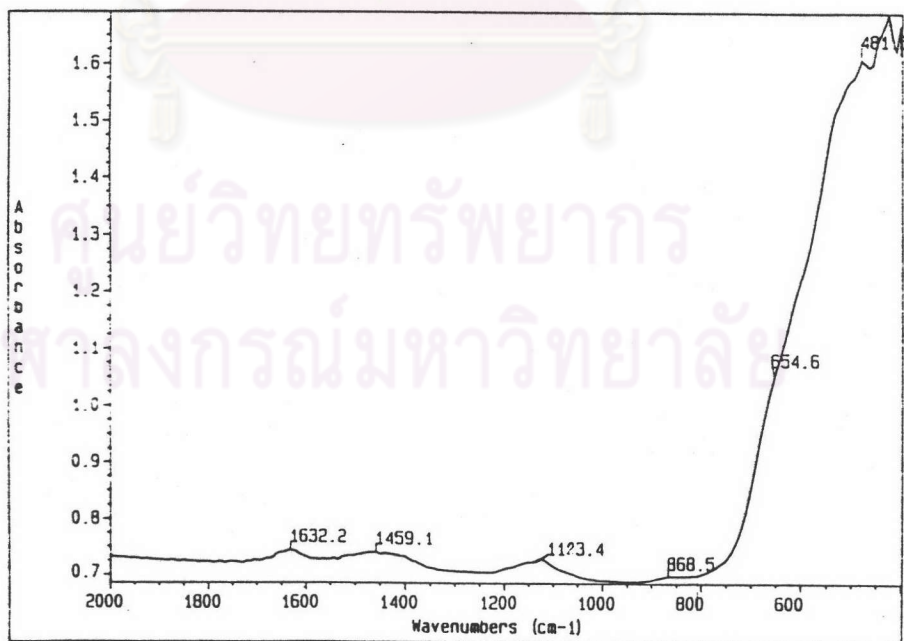


Figure 5.25 Infrared spectra of MgO

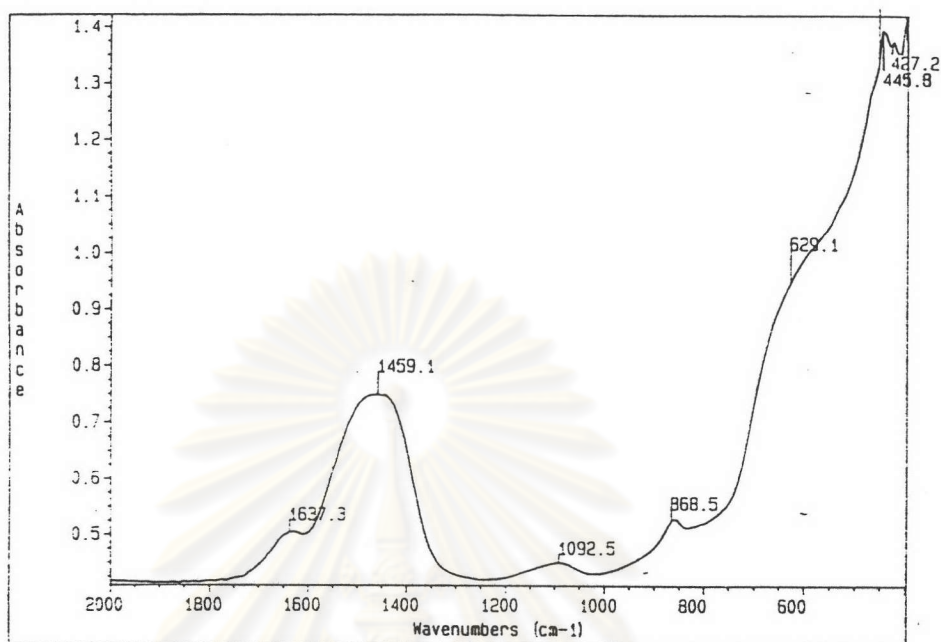


Figure 5.26 Infrared spectra of 4V-Mg-O

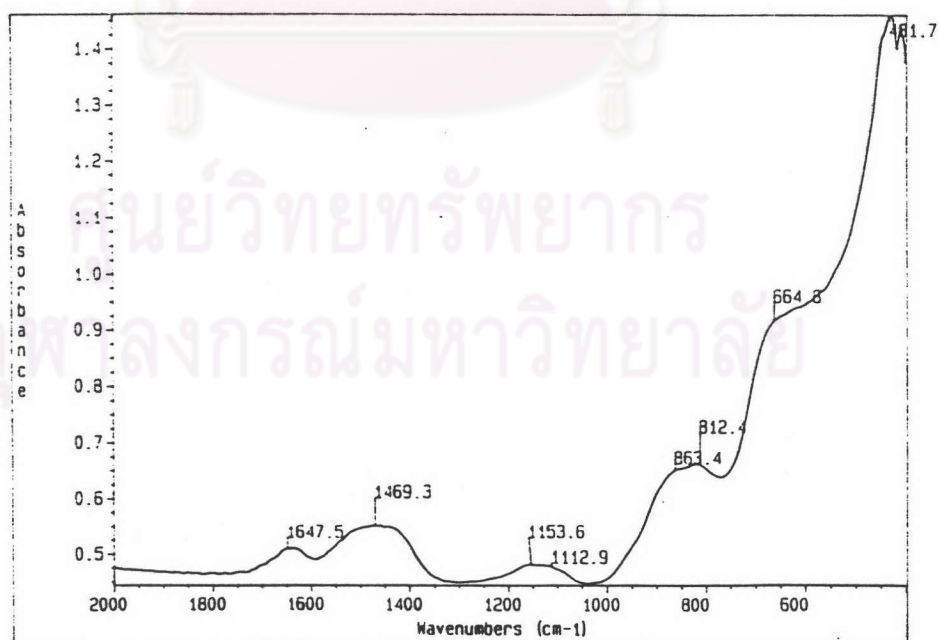


Figure 5.27 Infrared spectra of 21V-Mg-O

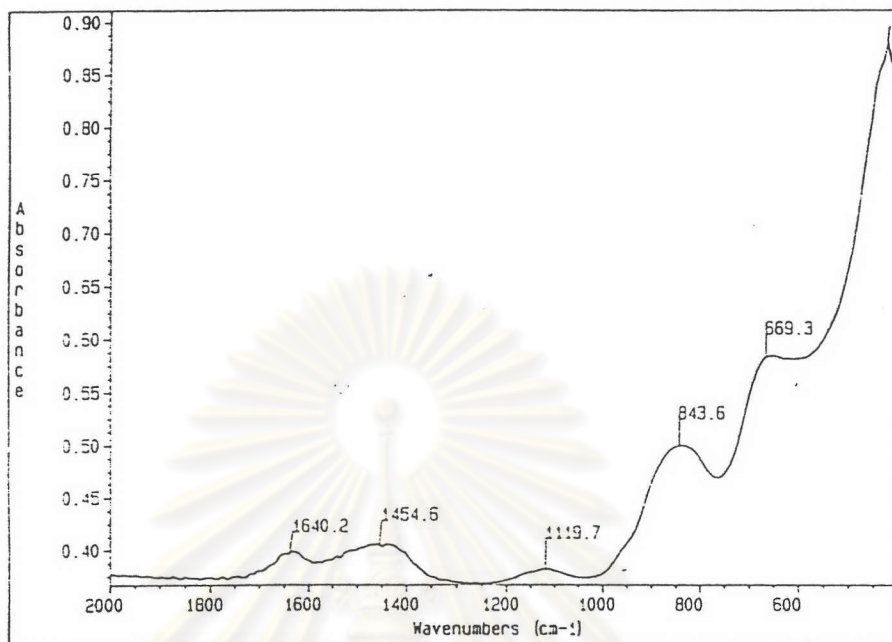


Figure 5.28 Infrared spectra of 28V-Mg-O

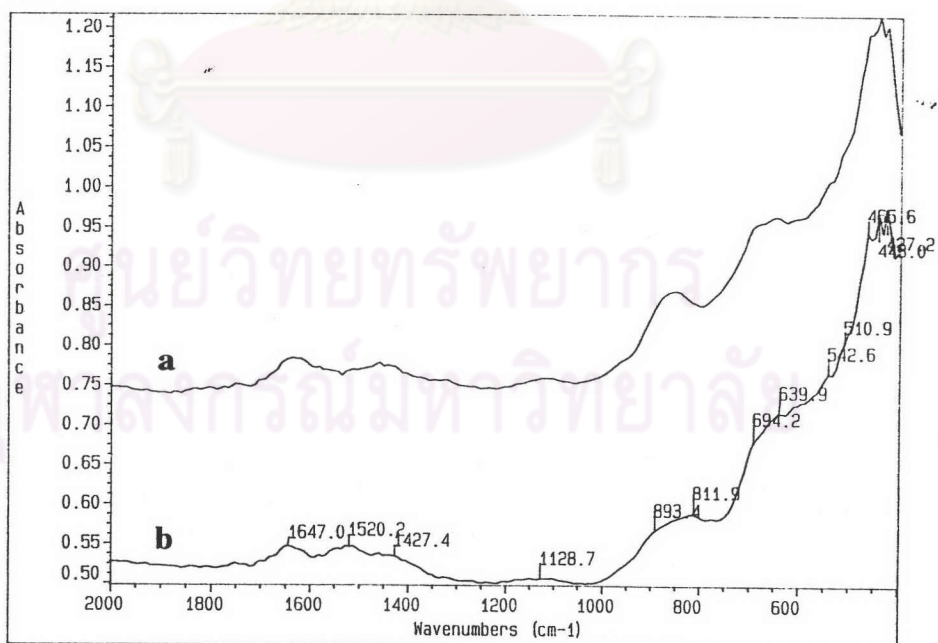


Figure 5.29 Infrared spectra of V-Mg-O catalysts which heated in the air at 550°C for 3 hrs: a) 21V-Mg-O, b) 28V-Mg-O.

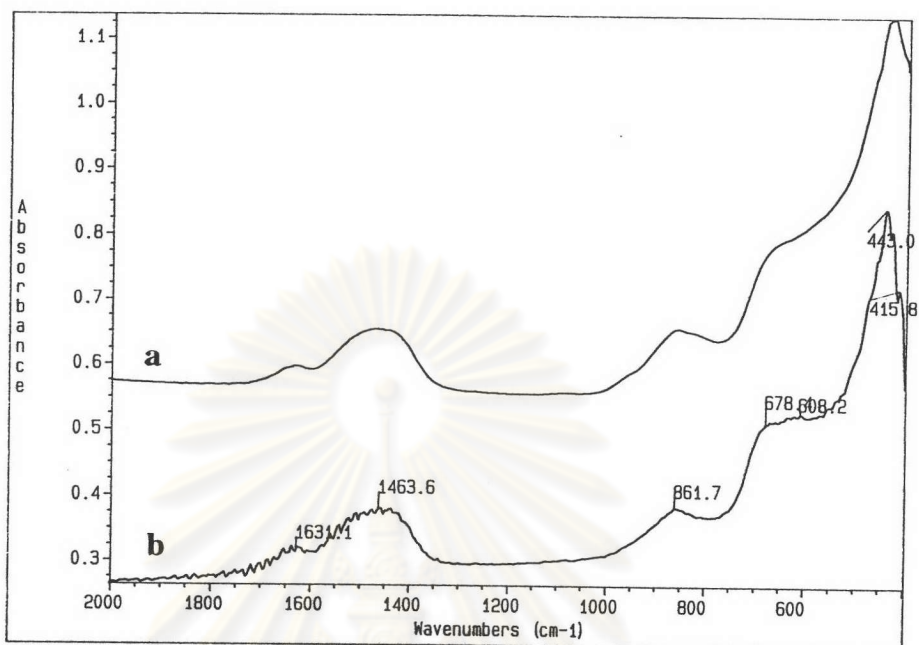


Figure 5.30 Infrared spectra of spent catalysts: a) 21V-Mg-O, b) 28V-Mg-O

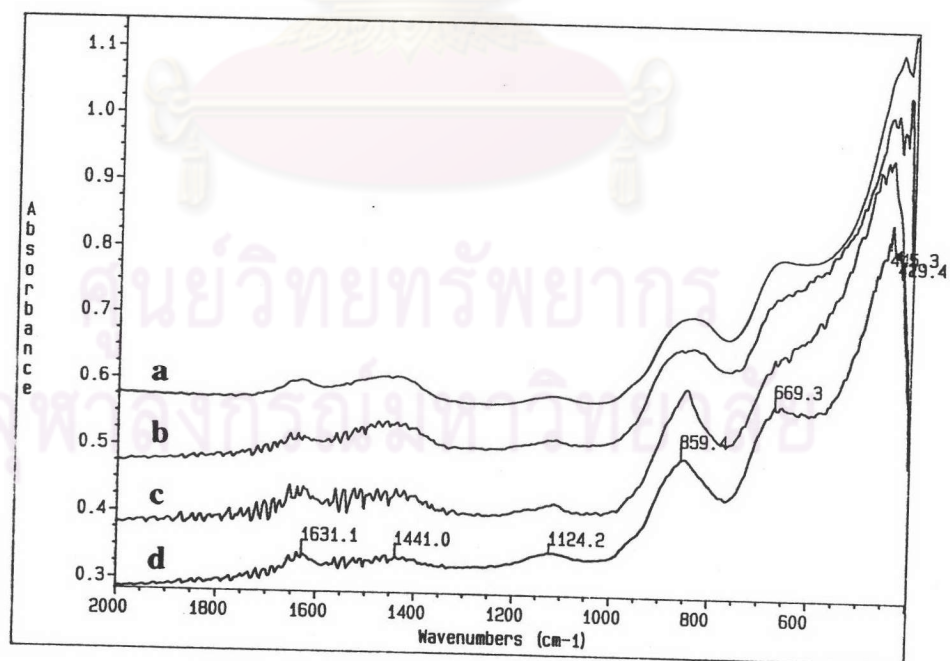


Figure 5.31 Infrared spectra of 28V-Mg-O(Na) catalysts: a) 28V-Mg-O, b) 28V-Mg-O(3%Na), c) 28V-Mg-O(2%Na), d) 28V-Mg-O(1%Na)

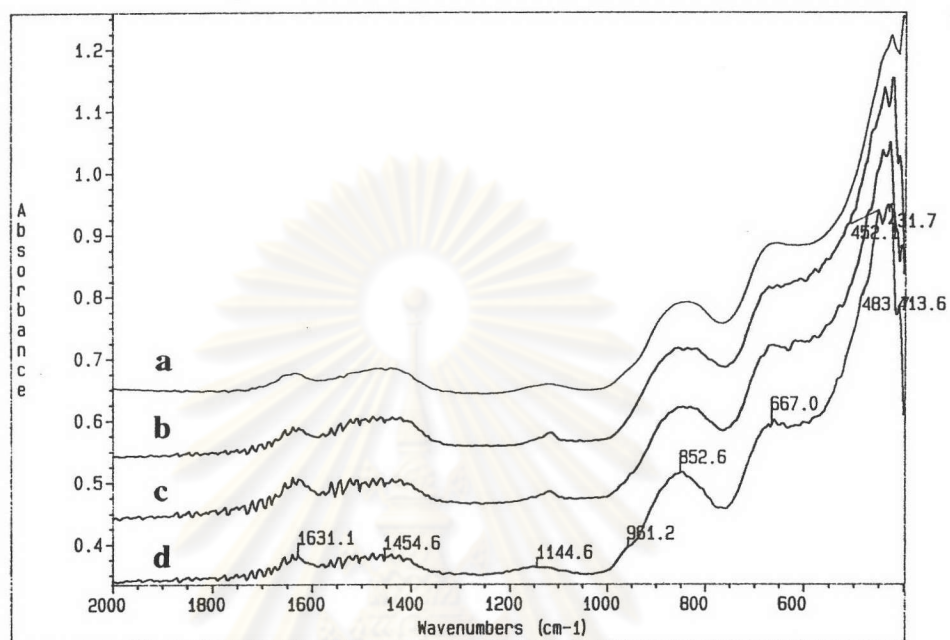


Figure 5.32 Infrared spectra of 28V-Mg-O(K) catalysts: a) 28V-Mg-O, b) 28V-Mg-O(3%K), c) 28V-Mg-O(2%K), d) 28V-Mg-O(1%K)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย