CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are classified into two major parts : the characterization of V-Mg-O catalyst and the catalytic reaction by the oxidative dehydrogenation of propane to propene.

5.1 Catalyst characterization

5.1.1 Determination of composition content of catalyst and surface area.

The results of 28 V-Mg-O catalyst and alkali metals loaded 28 V-Mg-O which are determined by AA and BET instrument are listed in table 5.1 below.

Table 5.1 The compositions of V-Mg-O catalysts and their BET surface areas.

catalyst	%V[b]	%Li[c]	%Na[c]	%K[c]	surface area(m^2/g)
28[a]V-Mg-O	28.3	-	-	-	60.7
28V-Mg-O (1%Li)	28.4	0.87	-	-	55.5
28V-Mg-O (2%Li)	28.1	1.93	-	-	36.6
28V-Mg-O (3%Li)	28.7	2.79	-	-	12.1
28V-Mg-O (1%Na)	28.4	-	1.04	-	60.1
28V-Mg-O (2%Na)	28.5	-	1.85	-	37.4
28V-Mg-O (3%Na)	28.2	-	2.99	-	35.7
28V-Mg-O (1%K)	28.1	-	-	0.99	58.5
28V-Mg-O (2%K)	28.2	-	-	2.03	42.4
28V-Mg-O (3%K)	27.9	-	-	3.27	33.7

[a] The number in the catalyst label denotes the approximate weight percentage of V calculated as V_2O_5.

[b] The content of vanadium is calculated in term of % by weight of V_2O_5.

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

The data in table 5.1 show that in all cases, 28 V-Mg-O provides the highest surface area. Furthermore, alkali adding affects the surface area of 28 V-Mg-O. It can be seen that the surface area of 28 V-Mg-O is declined significantly by alkali loading. This similar behaviour was reported by Kung et al. (1992) and Thammanonkul (1996). However, there is still no explanation about this phenomenon. Besides, surface area of 28 V-Mg-O is also decreased with increasing the content of alkali. The order of decreasing surface area of catalysts are as follows : Li > Na > K.

5.1.2 X-ray Diffraction (XRD)

X-ray Diffraction is a technique which can identify the crystal structure. Figure 5.1 illustrates XRD spectrum of V_2O_5. Three dominant peaks appear at the 2θ values of 20.5°, 26.5° and 31°. As presented in figure 5.2, the XRD spectrum of MgO shows two peaks at 43° and 62°. XRD spectrum of 28 V-Mg-O, presented in figure 5.3, shows peaks at the 2θ value of 43° and 62° which are the same positions as in the MgO spectrum. However, the peak of 28 V-Mg-O is broader than that of MgO because of the moisture in their structure [Thammanonkul (1996)]. Hence, it can be suggested that the structure of 28 V-Mg-O is similar to MgO, but more amorphous.

Moreover, it can be seen that V_2O_5 peak cannot be detected in the 28 V-Mg-O spectrum. That means the amount of vanadium oxides on 28 V-Mg-O surface may be not enough to be determined by XRD or the vanadium oxides did not form a V_2O_5 crystal structure on the MgO substrate. It is known that vanadium supported on MgO catalysts prefers to form a new compound containing V-Mg-O, not form vanadium oxides on Mg surface [Chaar et al. (1987), Sam et al. (1990)]. Besides, Gao et al. (1994b) reported that V-Mg-O catalyst containing around 28 wt.%V consists of Mg pyrovanadate and Mg orthovanadate. Thus, the unobservable diffraction lines of any V-Mg-O compounds such as $Mg_3V_2O_8$, MgV_2O_6, and $Mg_2V_2O_7$, indicates that possibly only very thin layer of some V-Mg-O compounds distributed on the surface of catalyst.

The XRD spectra for 28 V-Mg-O added with various alkali metals are shown in figures 5.4 to 5.12. All of alkali loaded 28 V-Mg-O have 2 peaks at the 2θ value of 43° and 62°. To compare with 28 V-Mg-O spectrum, all of alkali loaded 28 V-Mg-O have the same XRD spectra as 28 V-Mg-O. In the other hand, the crystal structure of alkali loaded catalyst is similar to that of 28V-Mg-O, due to the alkali content loaded is much less. However, some small peaks of 3 wt.% of Li (in figure 5.6) and Na (in figure 5.9)which are loaded on 28 V-Mg-O are obtained. It is possible that Li and Na in these samples may form LiO or NaO on the surface of 28 V-Mg-O, when the content of Li and Na loaded are high enough.

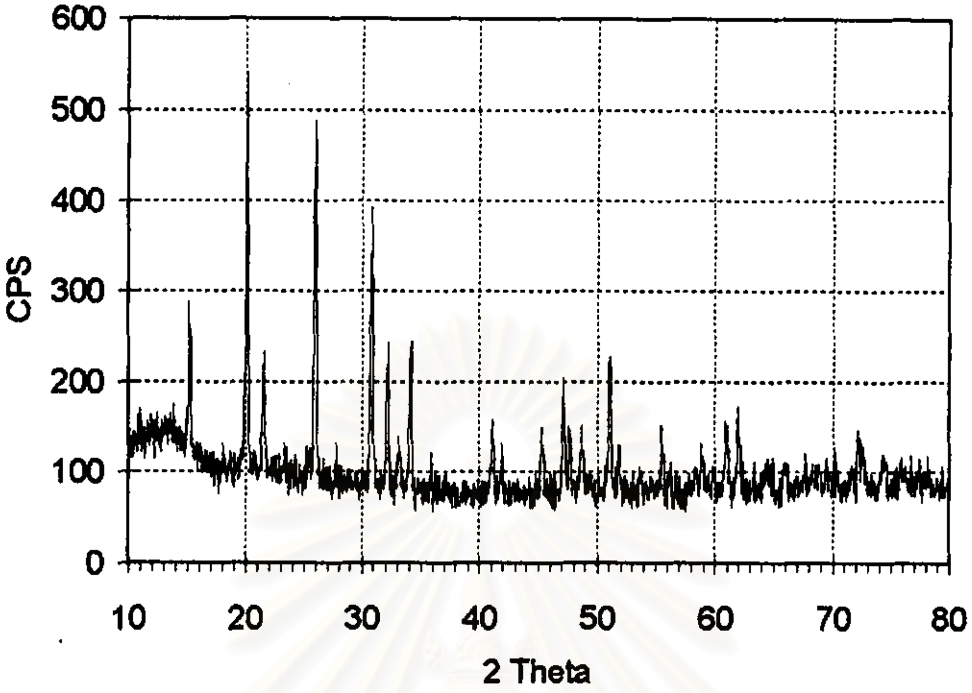

Figure 5.1 The XRD result of V_2O_5 catalyst.

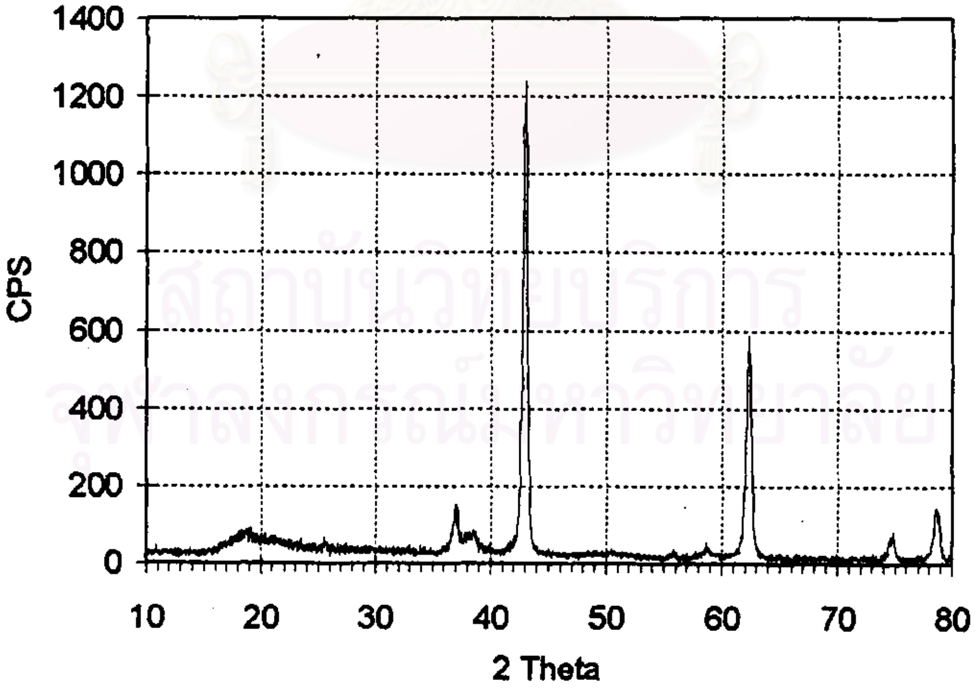

Figure 5.2 The XRD result of MgO catalyst.

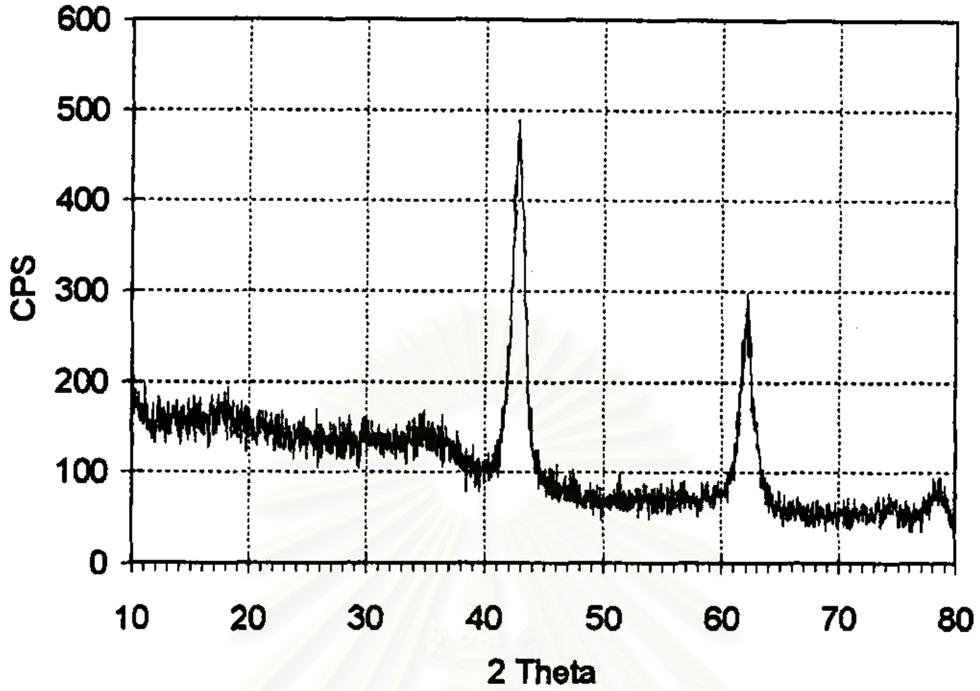

Figure 5.3 The XRD result of 28V-Mg-O catalyst.

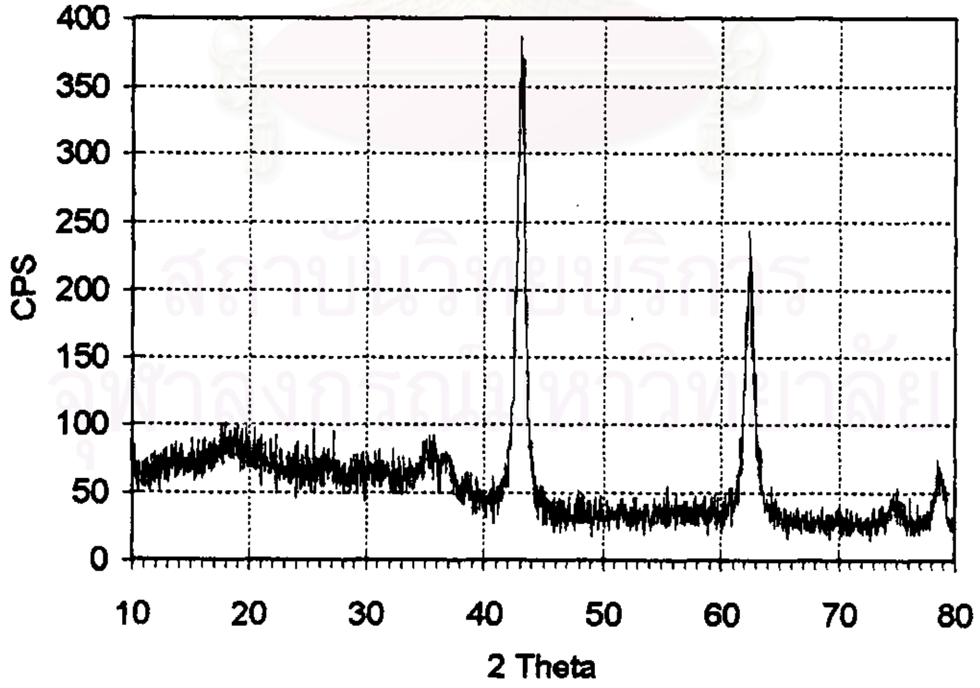

Figure 5.4 The XRD result of 28V-Mg-O (1%Li) catalyst.

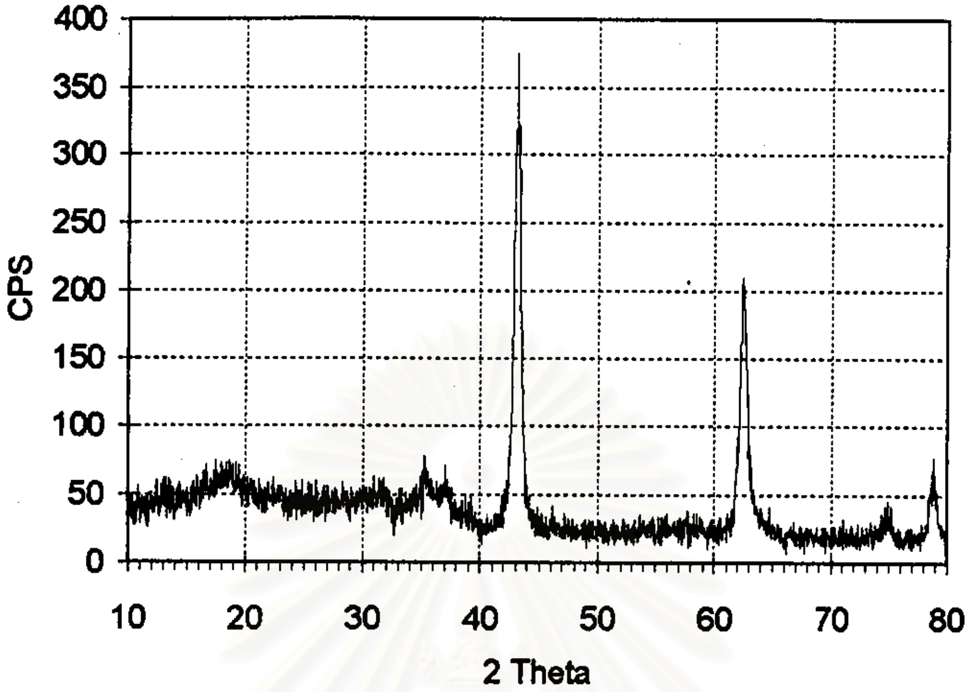

Figure 5.5 The XRD result of 28V-Mg-O (2%Li) catalyst

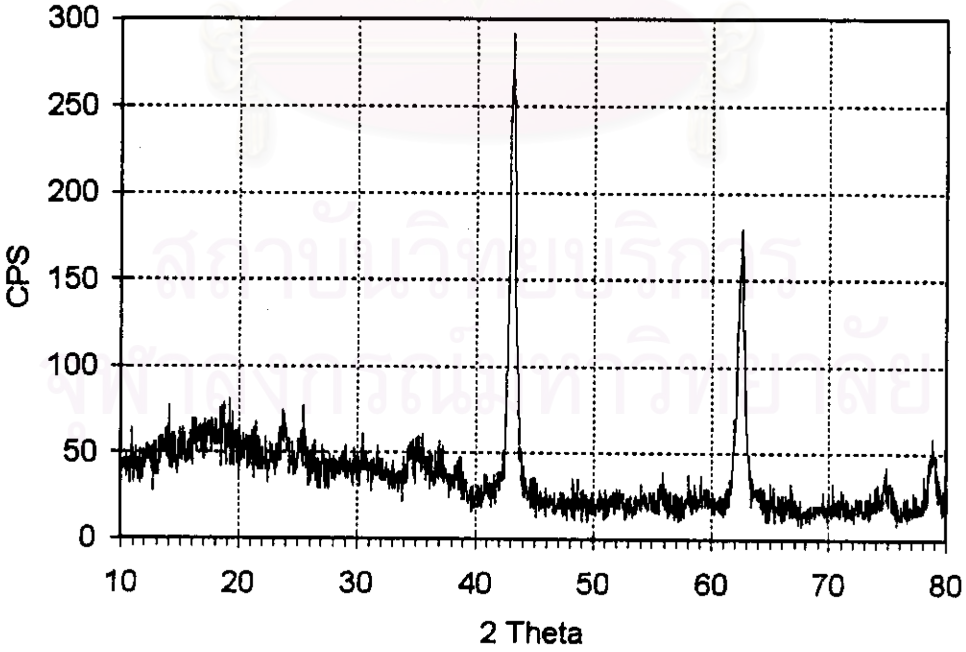

Figure 5.6 The XRD result of 28V-Mg-O (3%Li) catalyst

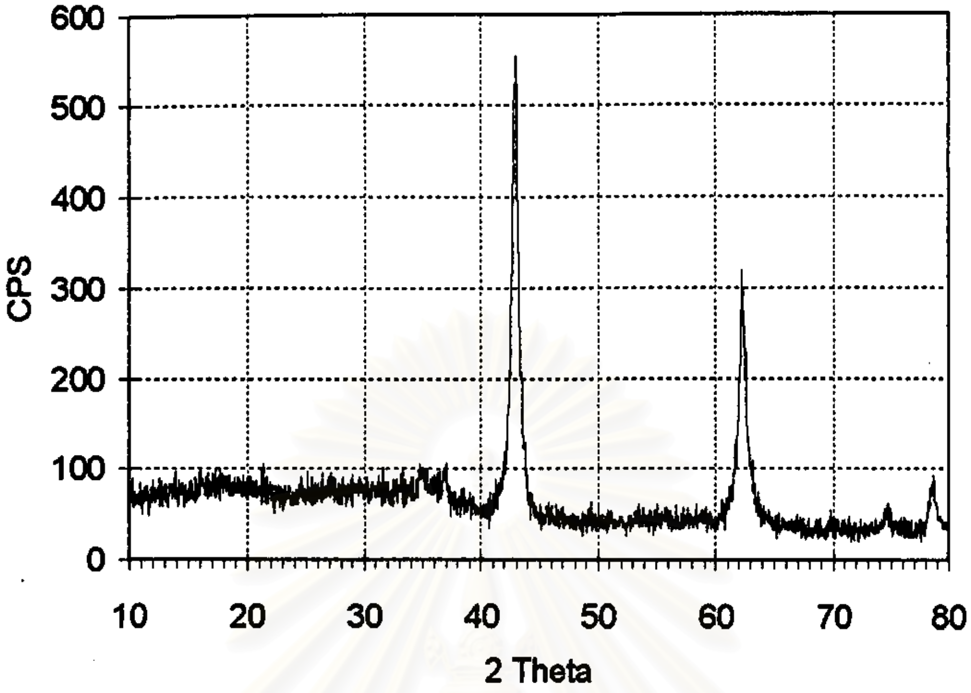

Figure 5.7 The XRD result of 28V-Mg-O (1%Na) catalyst

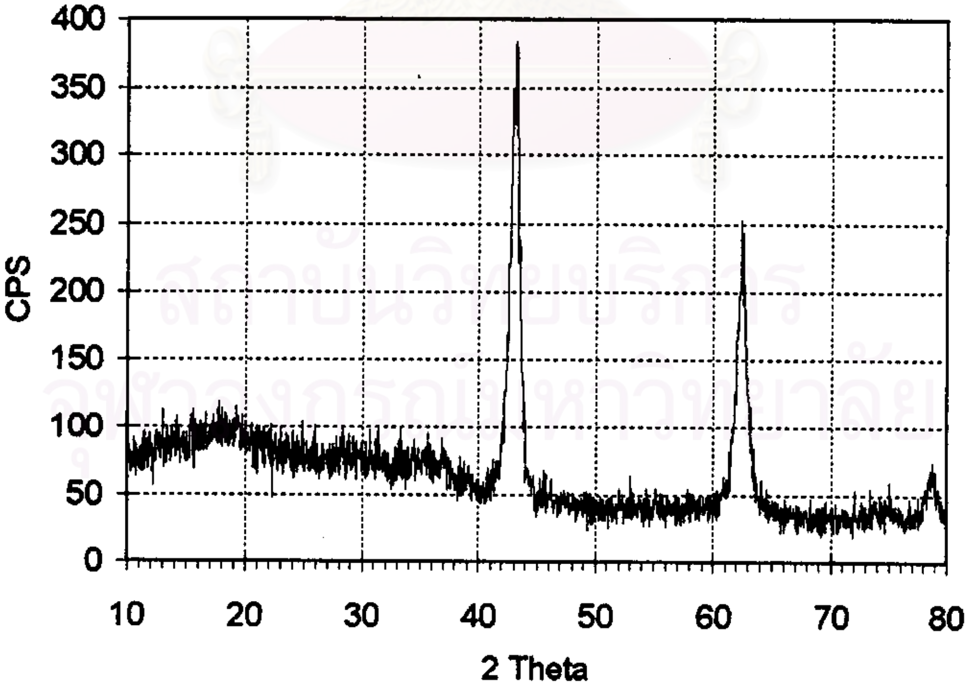

Figure 5.8 The XRD result of 28V-Mg-O (2%Na) catalyst

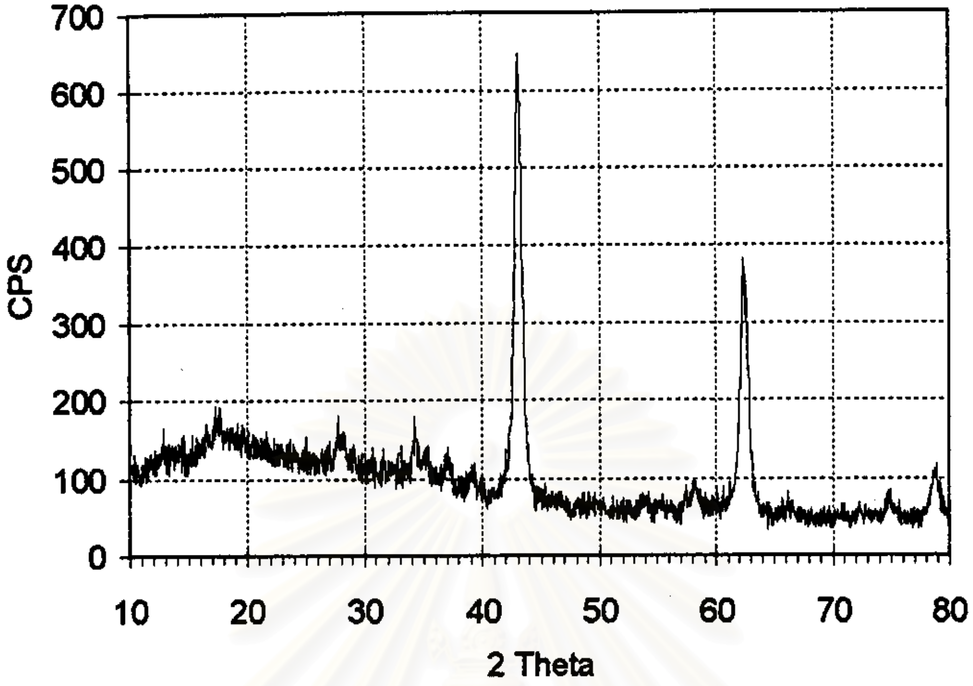

Figure 5.9 The XRD result of 28V-Mg-O (3%Na) catalyst

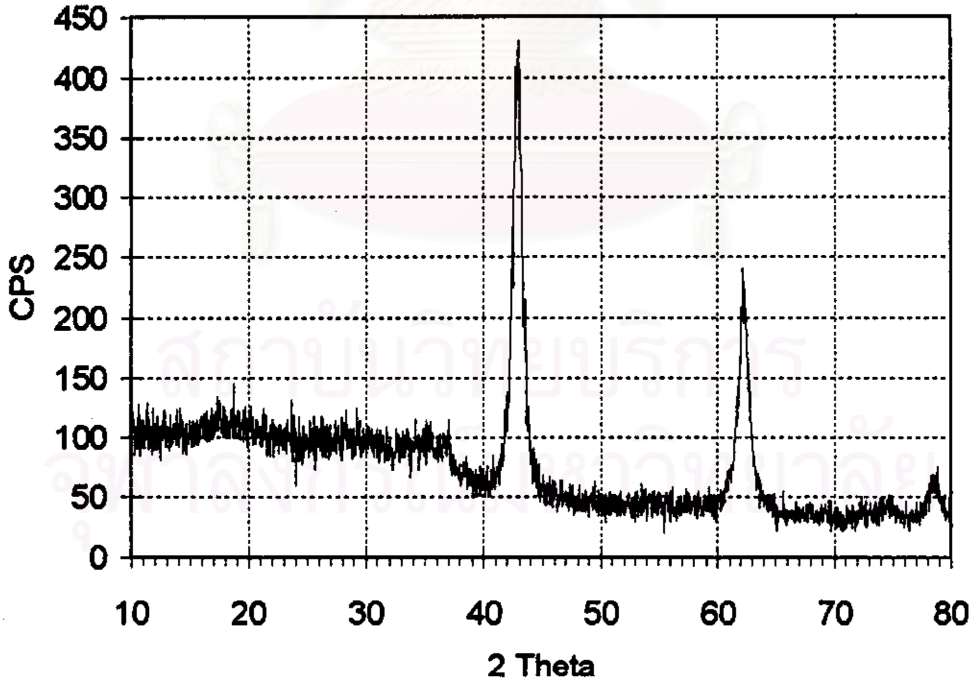

Figure 5.10 The XRD result of 28V-Mg-O (1%K) catalyst

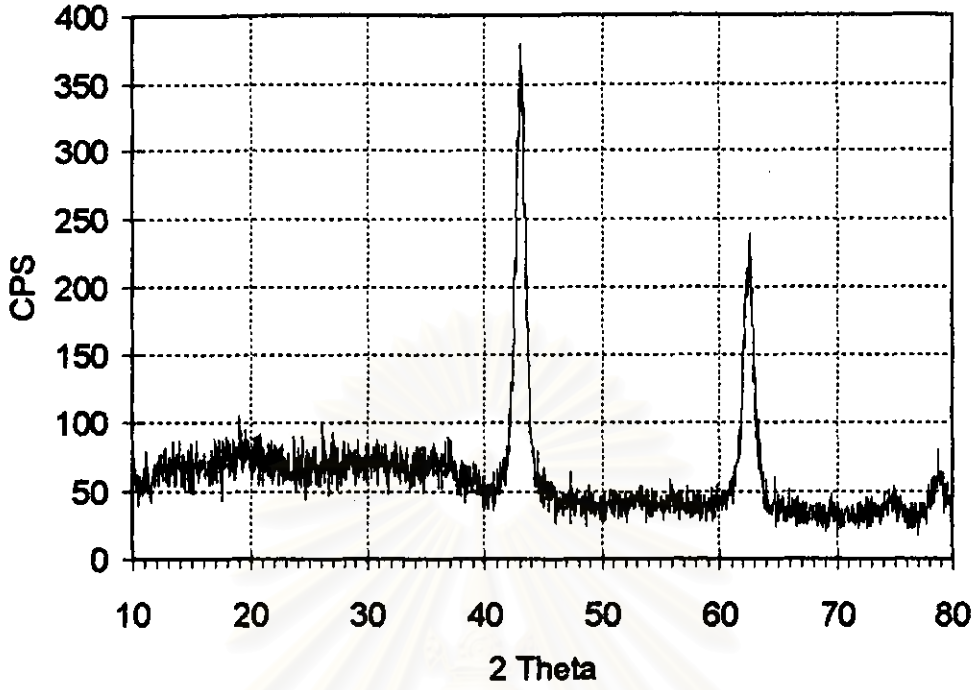

Figure 5.11 The XRD result of 28V-Mg-O (2%K) catalyst

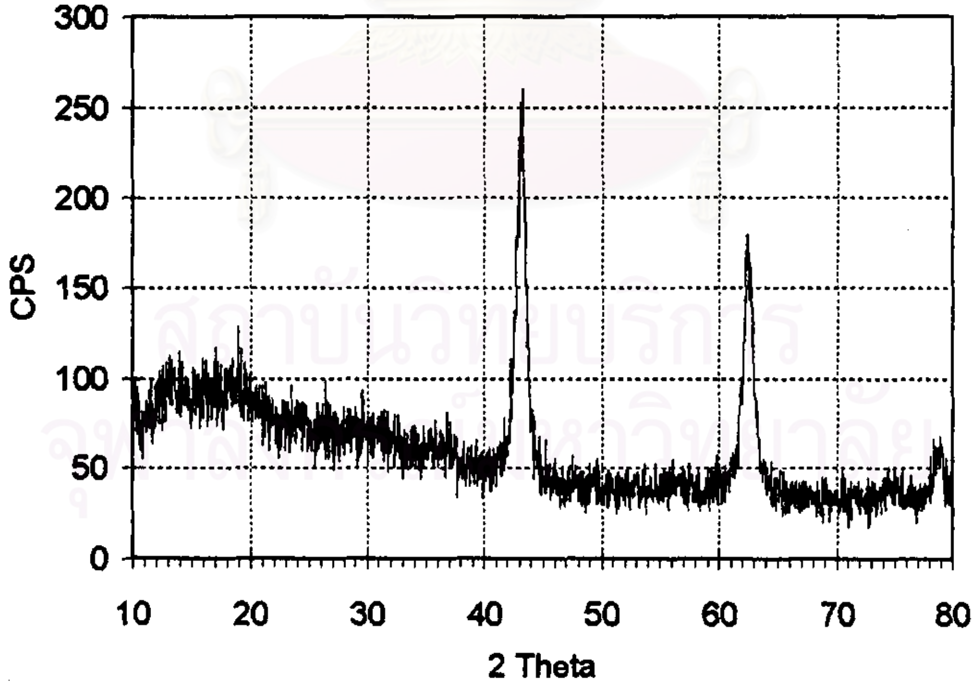

Figure 5.12 The XRD result of 28V-Mg-O (3%K) catalyst

5.1.3 Fourier Transform Infrared Spectrometer (FT-IR)

The functional group on the 28 V-Mg-O surface can be identified by using infrared radiation in the wavelength of 400-2000 cm^{-1} which is the proper wavelength for determining the solid surface.

The IR spectrum of 28 V-Mg-O is exhibited in figure 5.14. The position of a small peak around 1650 cm^{-1} is the peak of KBr which is the background peak. Additionally, the peak at around 860 cm^{-1} which can be assigned to short V=O bond in VO_3 species and the shoulder at around 660 cm^{-1} which can be assigned to V-O-V species, both belong to the Mg pyrovanadate compound [Busca et nal. (1994)], also appear in the 28 V-Mg-O spectrum. The structure of V_2O_7 unit in Mg pyrovanadate ($Mg_2V_2O_7$) is presented in figure 5.13 [Michalakos et al. (1993)]. Consequently, it can be concluded that the important species on 28 V-Mg-O surface are VO_3 species and V-O-V species.

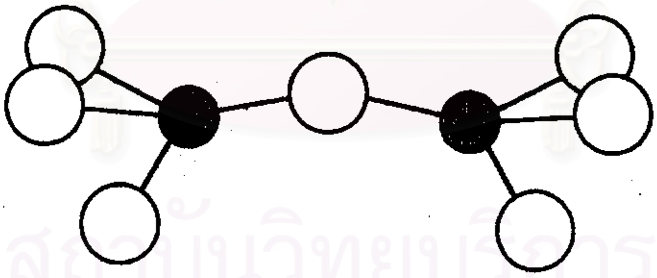

Figure 5.13 Schematic drawing of the active sites, V_2O_7 unit, in $Mg_2V_2O_7$.
○ - O ions, ● - V ions.

Figures 5.15 to 5.23 illustrate the IR spectra of 28 V-Mg-O loaded with various alkali metals. The spectra of all alkali loaded catalyst are similar to that of 28V-Mg-O except the V-O-V peak. It is found that the peak of V-O-V species at 660 cm^{-1} was disturbed by alkali loading. Nevertheless, there are no any effects on the peak of short V=O bond in VO_3 species at 860 cm^{-1}. When the alkali content is further increased up to 3 wt.%, the peak at 660 cm^{-1} of V-O-V species disappeared, while the peak at 860 cm^{-1} of VO_3 species tends to divide into 2 peaks, especially in 3 wt.%Li loaded 28 V-Mg-O. At this moment the phenomenon that the peak of VO_3 species splits into 2 peaks cannot be explained. Conclusively, the more increase the alkali content, the more loss the V-O-V species. From the above results, it is possible that alkali metal may form V-O-M and/or M-O-M structure on the catalyst surface apart from V-O-V species, where M is alkali.

In addition, for 28 V-Mg-O and alkali loaded 28 V-Mg-O, the absence of V=O peak which belongs to V_2O_5 at 1022 cm^{-1} in IR spectra is in good agreement with the results in the literature [Kryrov (1973)]. The XRD and IR spectra lead to the conclusion that the main surface structures of the unpromoted 28 V-Mg-O are VO_3 and V-O-V unit. The major structure of 28 V-Mg-O loaded alkali is also similar to that of the unpromoted 28 V-Mg-O, except the surface structure. On the surface of alkali loaded 28V-Mg-O, alkali tends to form V-O-M and/or M-O-M structure, where M is alkali. Besides, VO_3 species is also observed on their surfaces.

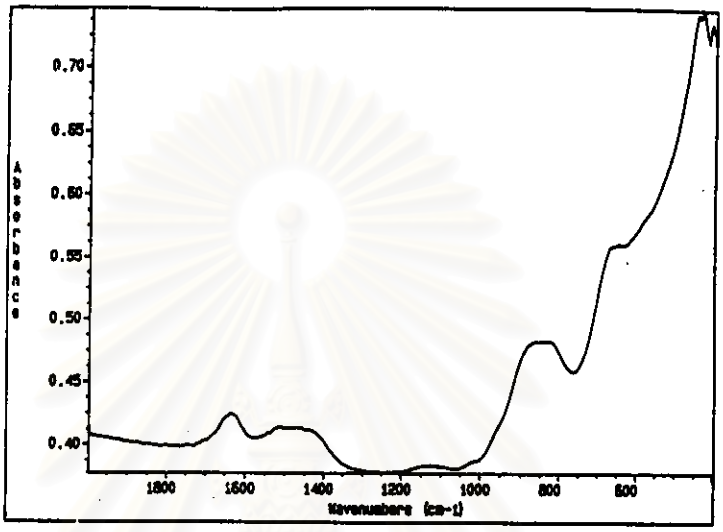

Figure 5.14 IR spectrum of 28V-Mg-O

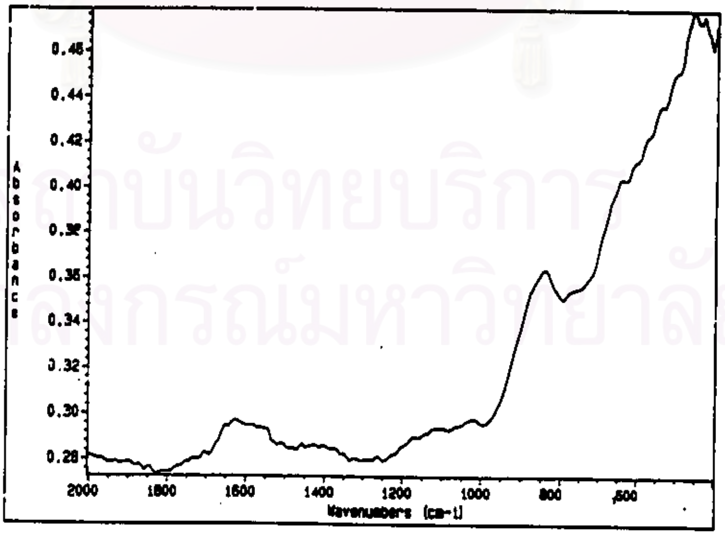

Figure 5.15 IR spectrum of 28V-Mg-O (1%Li)

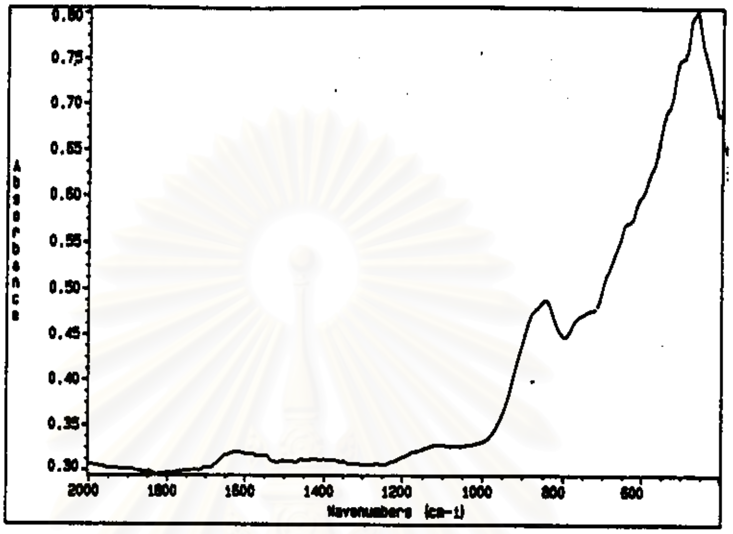

Figure 5.16 IR spectrum of 28V-Mg-O (2%Li)

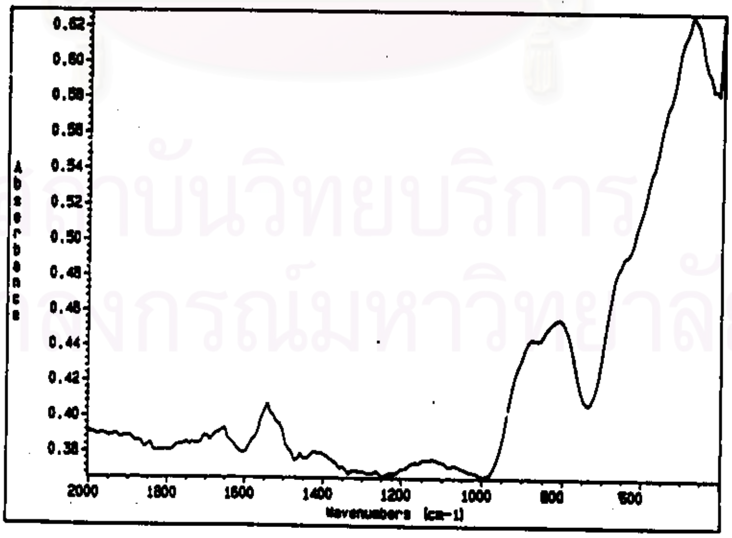

Figure 5.17 IR spectrum of 28V-Mg-O (3%Li)

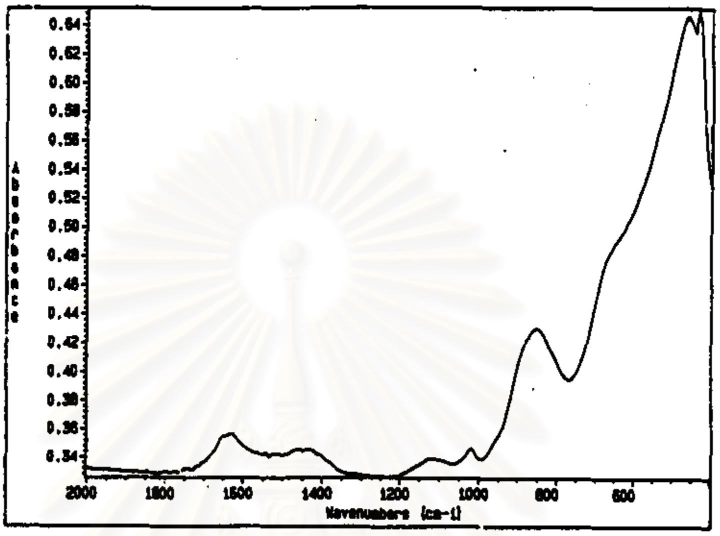

Figure 5.18 IR spectrum of 28V-Mg-O (1%Na)

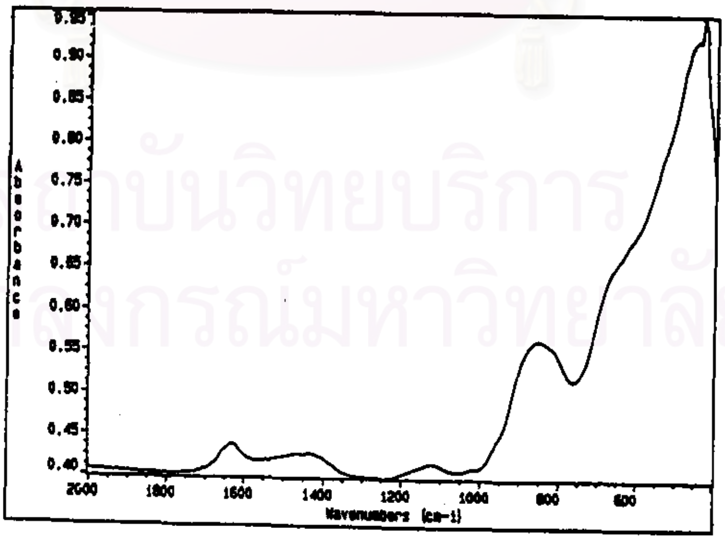

Figure 5.19 IR spectrum of 28V-Mg-O (2%Na)

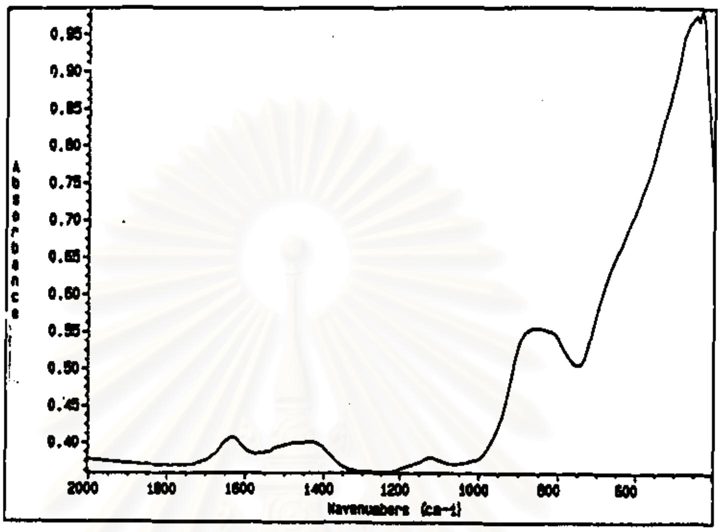

Figure 5.20 IR spectrum of 28V-Mg-O (3%Na)

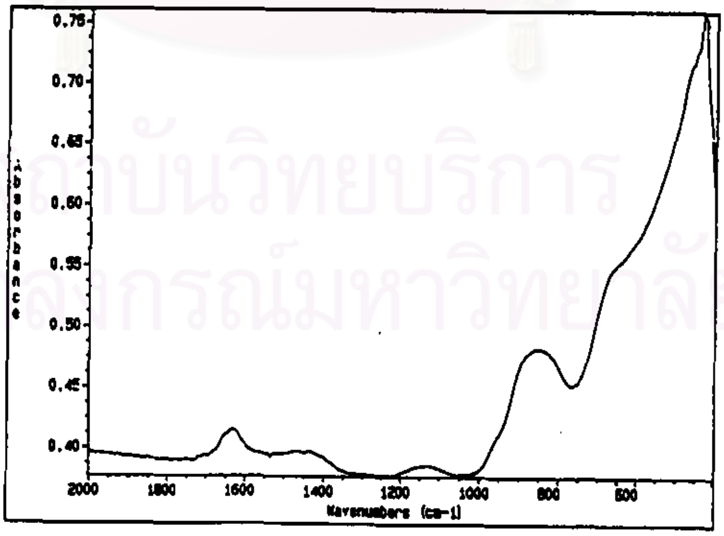

Figure 5.21 IR spectrum of 28V-Mg-O (1%K)

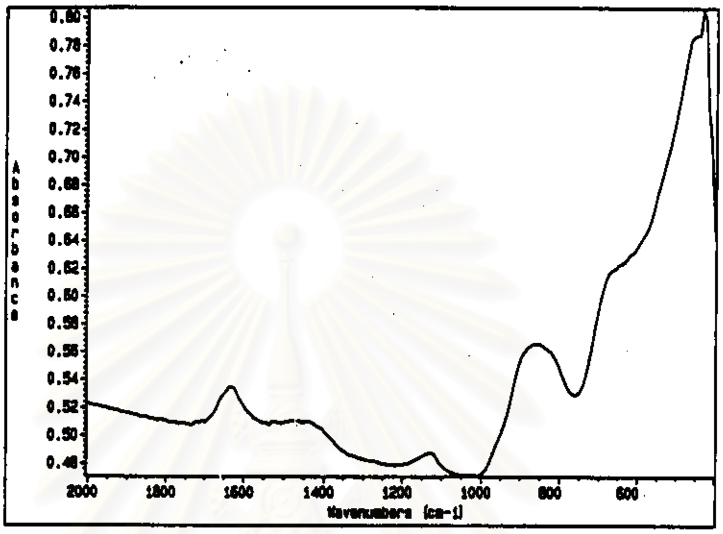

Figure 5.22 IR spectrum of 28V-Mg-O (2%K)

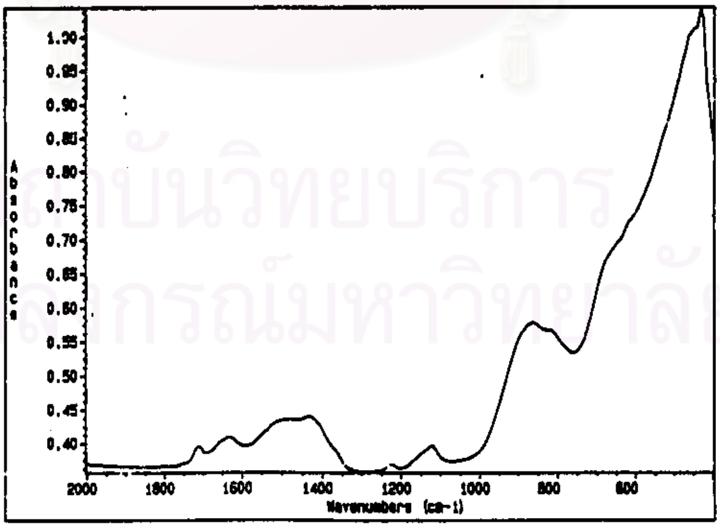

Figure 5.23 IR spectrum of 28V-Mg-O (3%K)

5.1.4 Thermogravimetric analysis (TGA)

The loss of catalyst species, as in heating program, can be determined in term of weight loss by using thermogravimetric analysis. Each thermogram consists of three curves : temperature curve, weight curve and differentiate weight (dtg) curve.

For the V-Mg-O catalyst, the presence of some moisture covered on the catalyst surface has been proposed [Vedrine et al. (1996)]. From TGA result of 28V-Mg-O (figure 5.24), two weight loss steps in the temperature range of 50-200 °C and 200-370 °C can be observed. In figures 5.25 to 5.27, the lost of weight in Li loaded 28V-Mg-O is not significant. While the weight losses of Na and K loaded 28V-Mg-O as presented in figures 5.28 to 5.33 are more noticeable. However, the TGA results of Na and K loaded 28V-Mg-O still show the same weight loss steps as of unpromoted 28V-Mg-O. It is possible that when the catalyst is heated up to the experiment temperature, the species such as the moisture can be desorbed from the catalyst structure.

Considering of all TGA thermograms, the loss of weight is not evident in both 28V-Mg-O and alkali loaded 28V-Mg-O. It may be limitation of catalyst content in TGA measurement. The catalyst, therefore, are investigated by using temperature programmed decomposition (TPD) for identifying species desorbed.

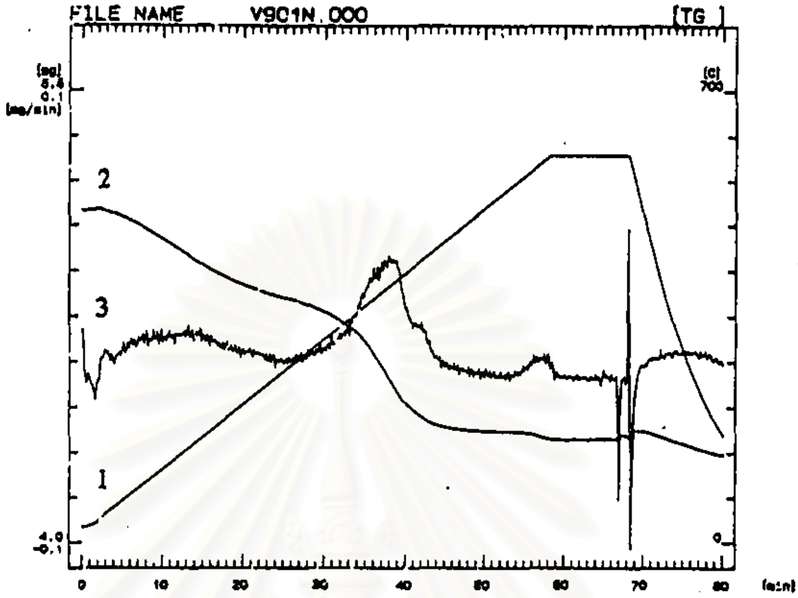

Figure 5.24 TGA thermogram of 28V-Mg-O, which 1 is temperature, 2 is weight and 3 is differential weight

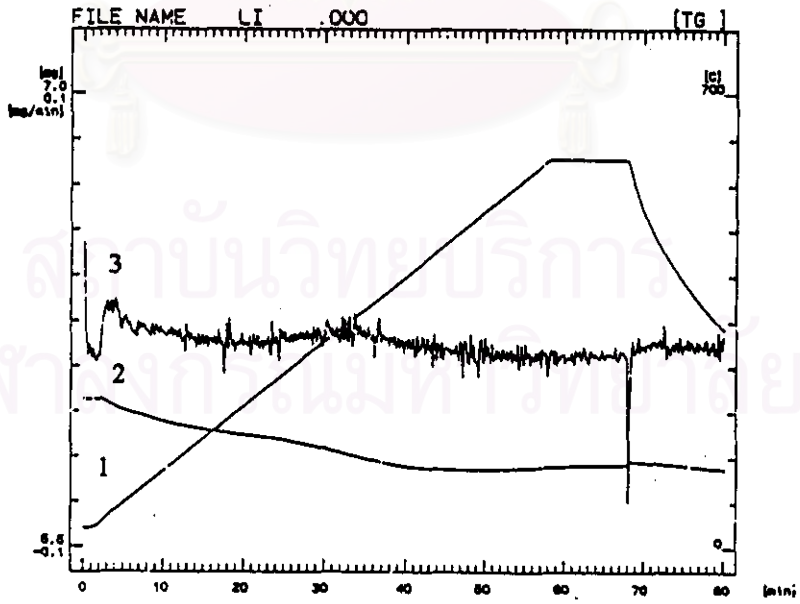

Figure 5.25 TGA thermogram of 28V-Mg-O(1%Li) , which 1 is temperature, 2 is weight and 3 is differential weight

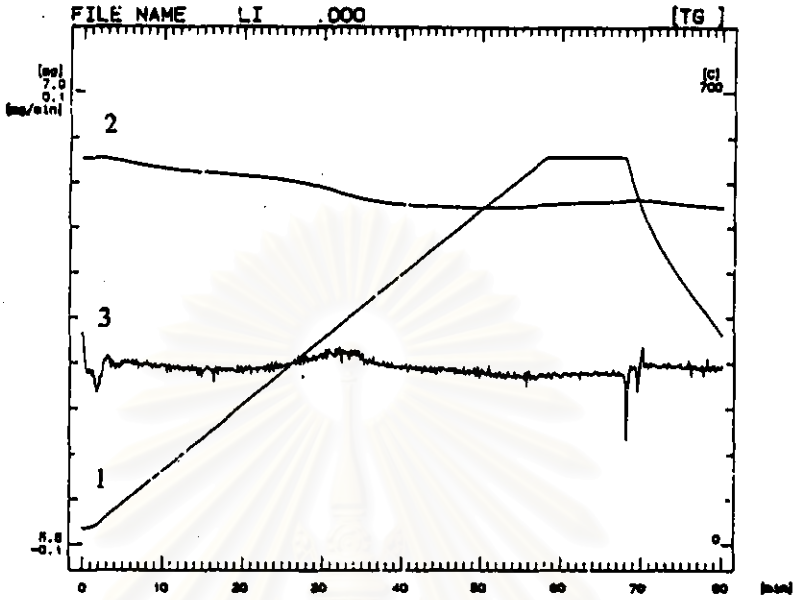

Figure 5.26 TGA thermogram of 28V-Mg-O(2%Li) , which 1 is temperature, 2 is weight and 3 is differential weight

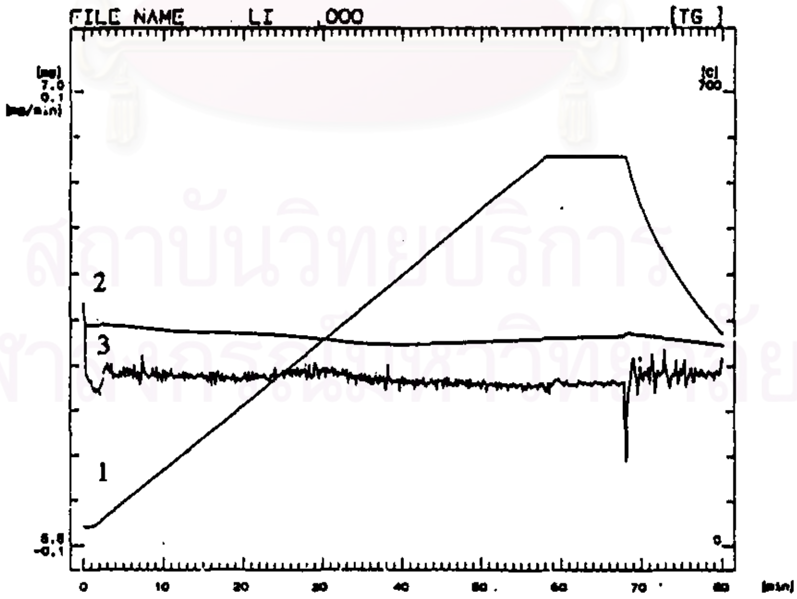

Figure 5.27 TGA thermogram of 28V-Mg-O(2%Li) , which 1 is temperature, 2 is weight and 3 is differential weight

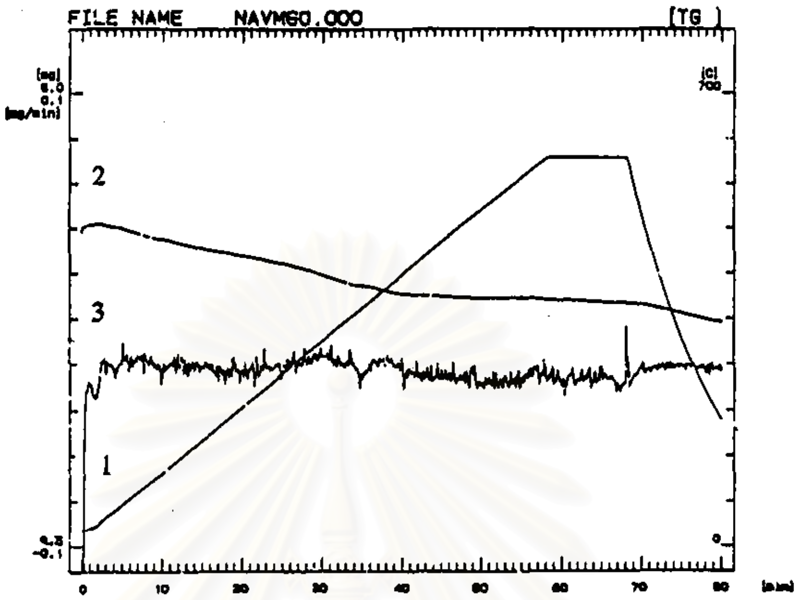

Figure 5.28 TGA thermogram of 28V-Mg-O(1%Na) , which 1 is temperature, 2 is weight and 3 is differential weight

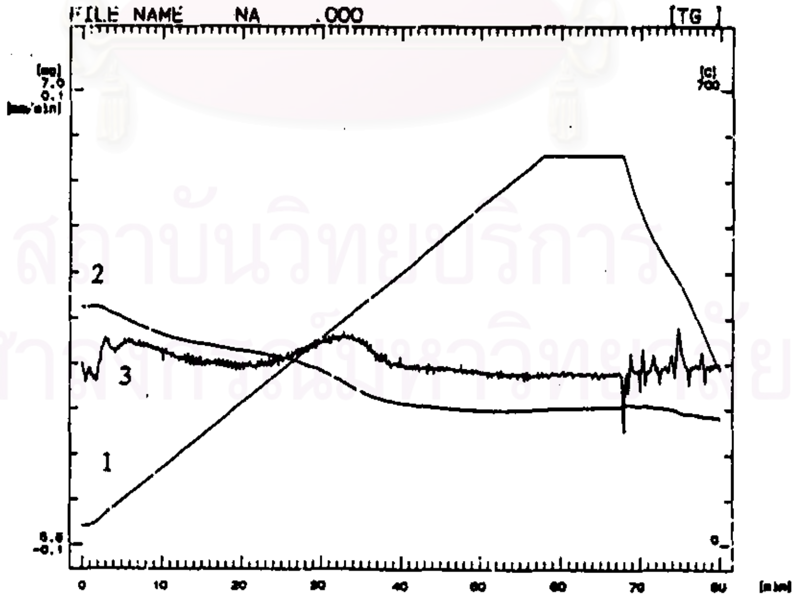

Figure 5.29 TGA thermogram of 28V-Mg-O(2%Na) , which 1 is temperature, 2 is weight and 3 is differential weight

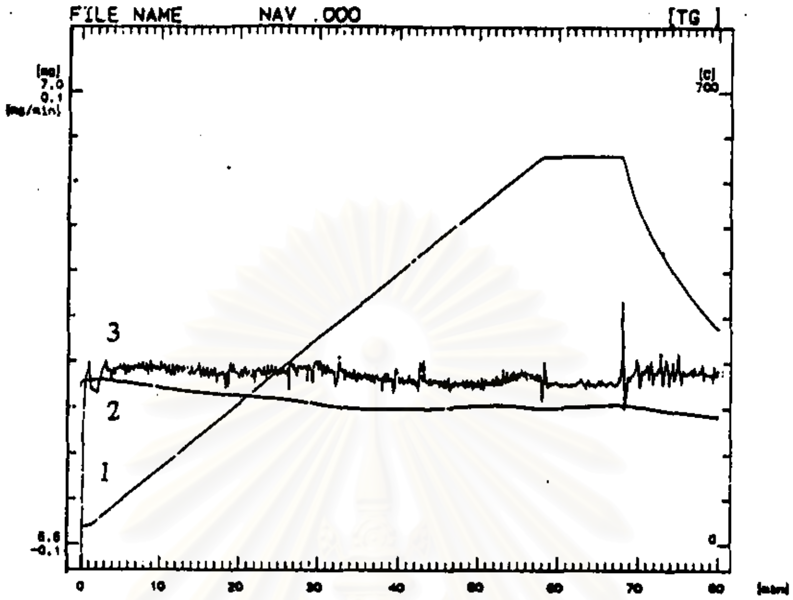

Figure 5.30 TGA thermogram of 28V-Mg-O(3%Na) , which 1 is temperature, 2 is weight and 3 is differential weight

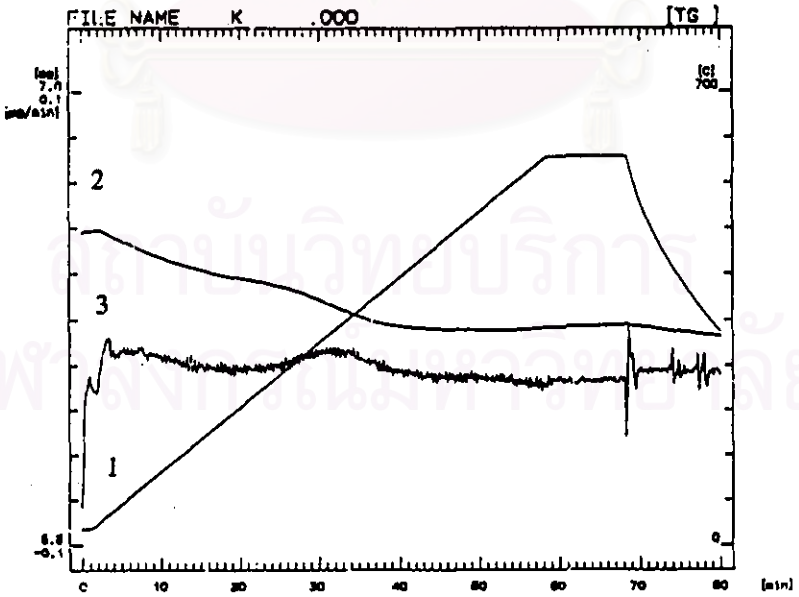

Figure 5.31 TGA thermogram of 28V-Mg-O(1%K) , which 1 is temperature, 2 is weight and 3 is differential weight

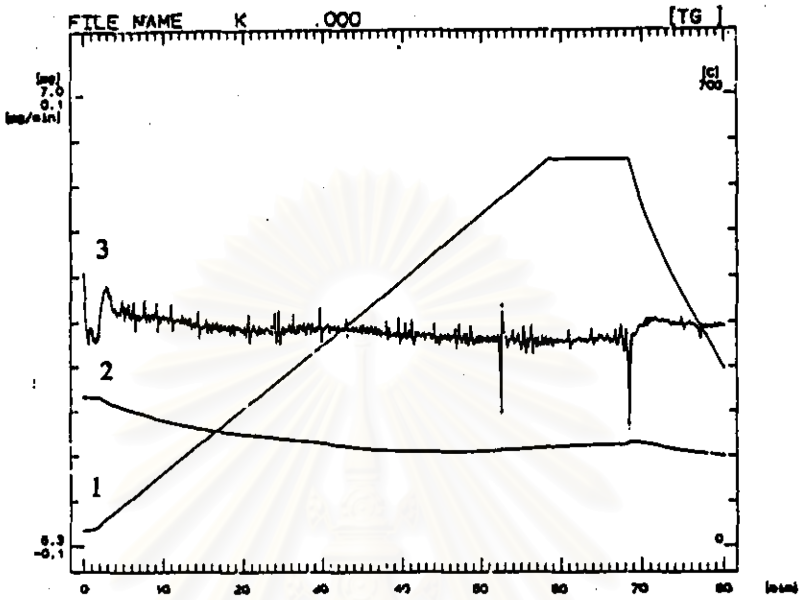

Figure 5.32 TGA thermogram of 28V-Mg-O(2%K) , which 1 is temperature, 2 is weight and 3 is differential weight

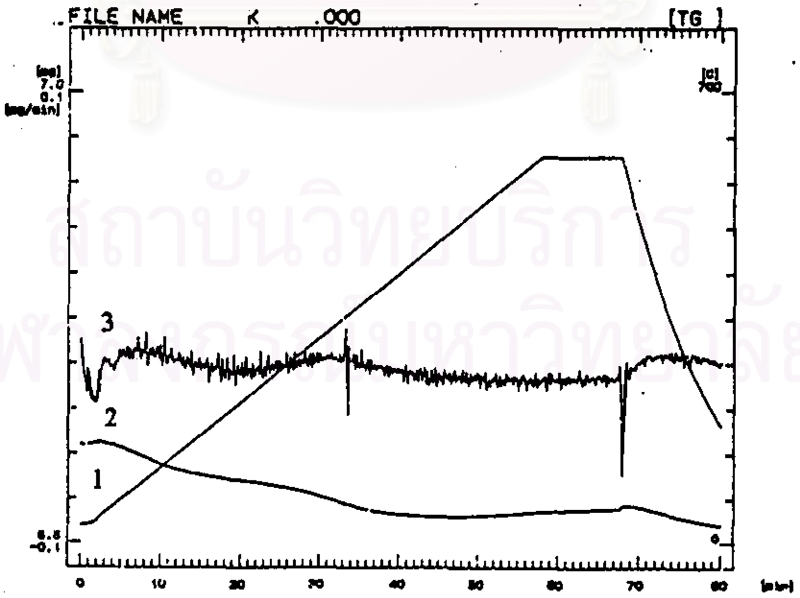

Figure 5.33 TGA thermogram of 28V-Mg-O(3%K) , which 1 is temperature, 2 is weight and 3 is differential weight

5.1.5 Temperature programmed decomposition (TPD)

This technique is able to identify species which decompose from catalyst at different temperatures. The outlet gas is analyzed by a GC equipped with TCD. The species in the outlet gas , consists of H_2O and O_2 , in terms of peak area as a function of temperature are illustrated in figures 5.34 to 5.43. It is found that H_2O is the main species lost from the catalysts accompanied with a small amount of O_2.

Considering of H_2O, on 28 V-Mg-O and alkali metal loaded 28 V-Mg-O, it can be observed that H_2O loss from catalysts at the broad peaks around 50-250°C and 250-400°C. The first peak is likely to be the desorption of moisture from the catalyst surface, which assigned to H_2O physical adsorption. The second one, which occurs at the temperature range of the 250-400°C, may be the moisture in the bulk of catalyst structure.

From the TPD results of 28 V-Mg-O, one can see that the area of the peak at 50-250°C is greater than that of at 250-400°C. This means that the moisture adsorbed on the surface of 28 V-Mg-O is more than the moisture adsorbed in the bulk of 28 V-Mg-O.

TPD results obtained from 28 V-Mg-O loaded with alkali metal (Li, Na, K) also show similar phenomenon. In figures 5.35 to 5.43, two broad peaks which are at the same position as in the TPD results of 28 V-Mg-O can be seen. However, in contrast to 28 V-Mg-O, the second peak of alkali metal loaded 28 V-Mg-O increases to be almost equal to the first peak, except that of Na loaded 28 V-Mg-O. In the case of 28 V-Mg-O (2%Na), the area of the second peak is two times greater than that of 28 V-Mg-O (1%Na), as well as 28 V-Mg-O (3%Na), which the area of second peak is three times more than that of 28V-Mg-O (1%Na). From the fact that sodium oxides prefer to adsorb some moisture, it is possible that the more the Na content, the more the H_2O adsorb. In conclusion, alkali metal loading on 28 V-Mg-O enhances H_2O adsorption in the bulk of catalyst structure.

It is known that V-Mg-O catalyst is an oxide catalyst which consists of oxygen in their structure. Hence, when 28V-Mg-O catalyst as in figure 5.34 is heated in inert atmosphere, oxygen gas can desorb constantly from 28V-Mg-O structure, while 1 wt.% alkali loading in 28 V-Mg-O (see in figures 5.35, 5.38 and 5.41), the desorption of oxygen species will rapidly increase. When increasing the amount of alkali loading in 28V-Mg-O, oxygen species can be desorbed from the catalyst surface, that means the catalyst surface is easy to be reduced. However, for the more amount of alkali loading in 28V-Mg-O , the desorption of oxygen does not depend on the temperature of the experiment.

Additionally, sometimes it can be found that H_2O adsorption depends on the preserve of catalyst, but the O_2 adsorption.

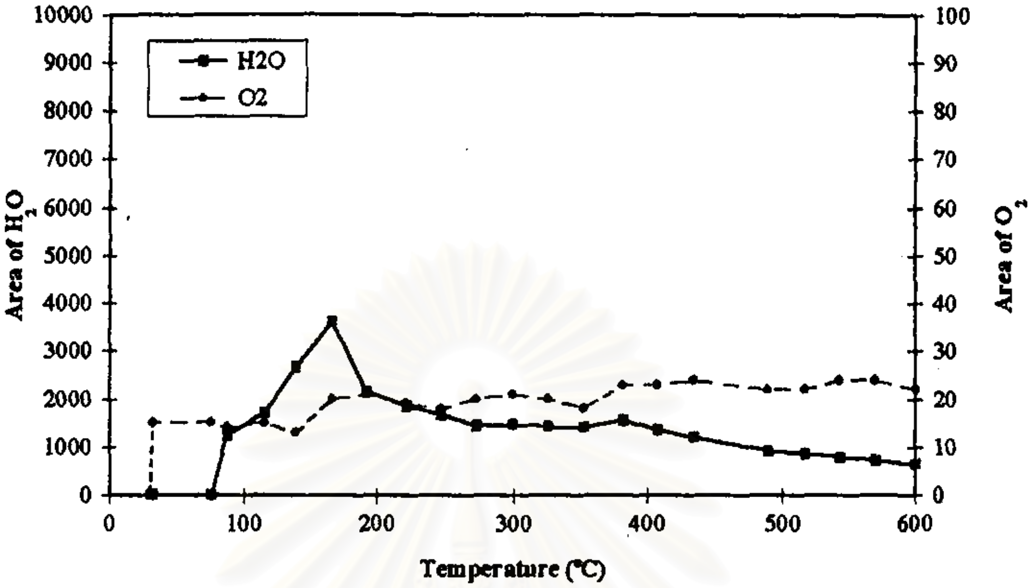

Figure 5.34 Temperature programmed decomposition of 28V-Mg-O

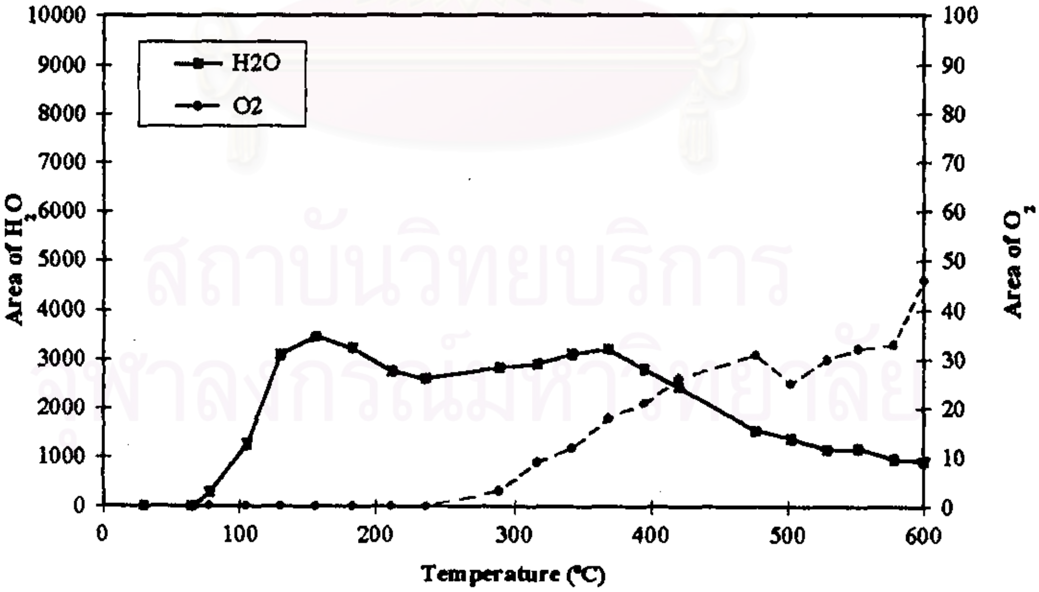

Figure 5.35 Temperature programmed decomposition of 28V-Mg-O (1%Li)

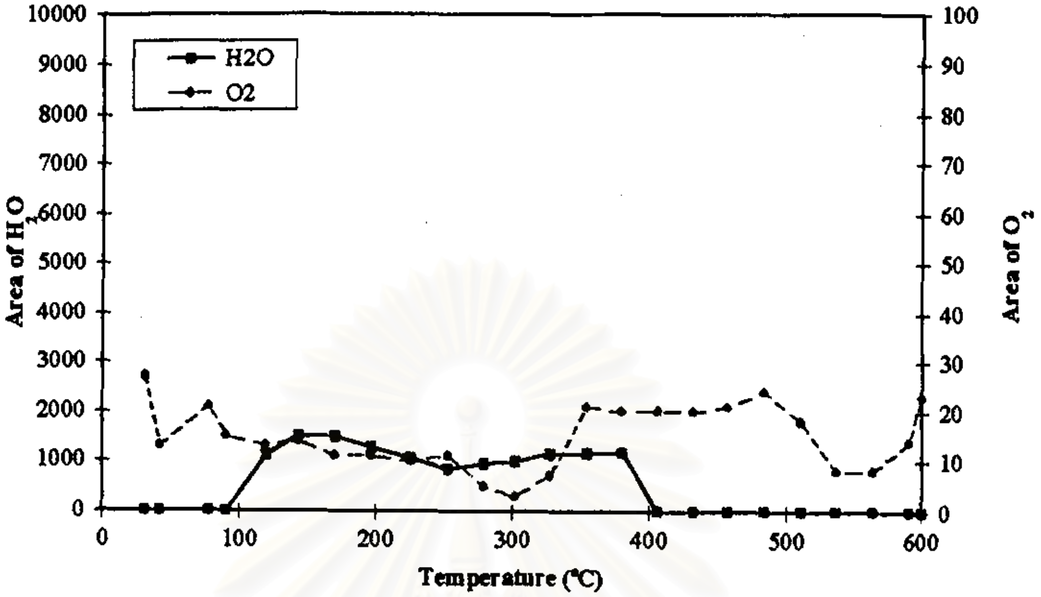

Figure 5.36 Temperature programmed decomposition of 28V-Mg-O (2%Li)

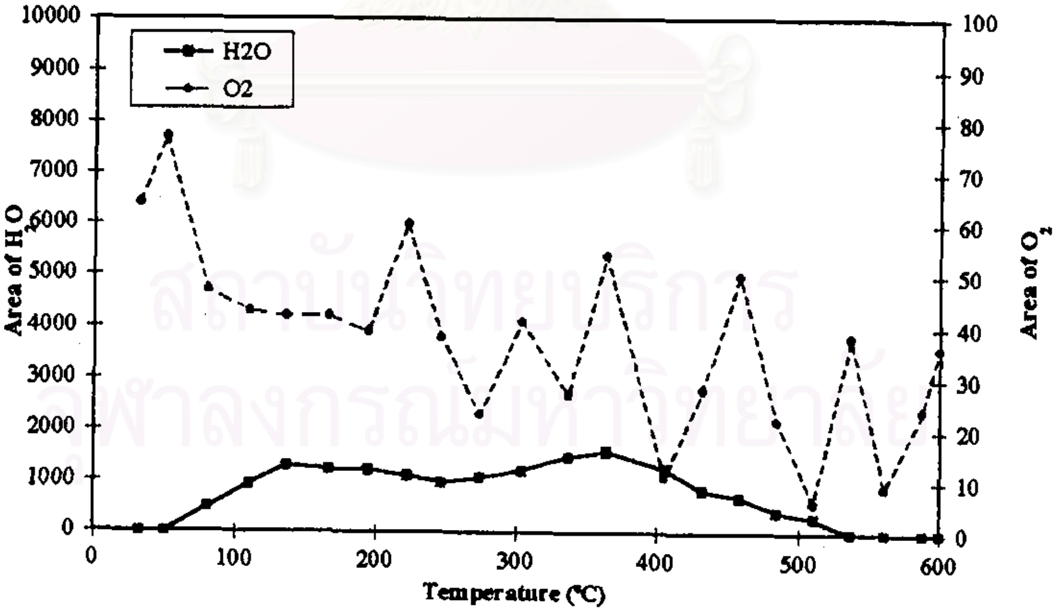

Figure 5.37 Temperature programmed decomposition of 28V-Mg-O (3%Li)

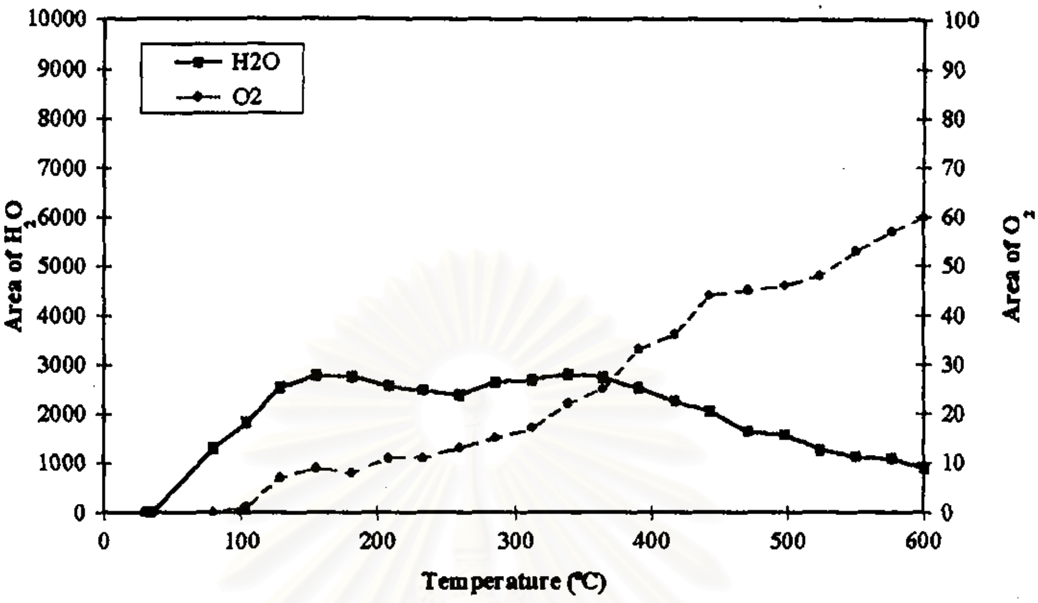

Figure 5.38 Temperature programmed decomposition of 28V-Mg-O (1%Na)

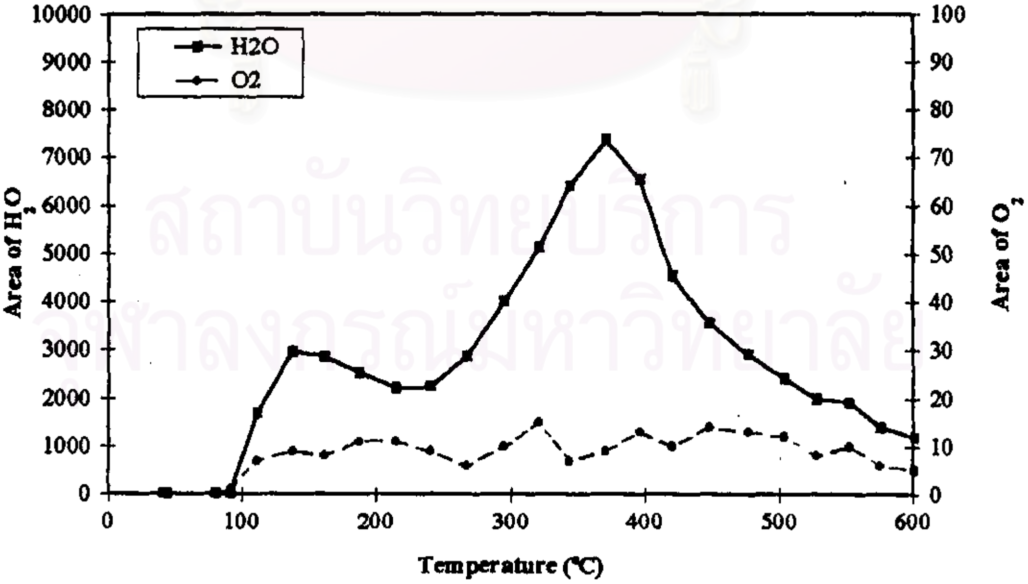

Figure 5.39 Temperature programmed decomposition of 28V-Mg-O (2%Na)

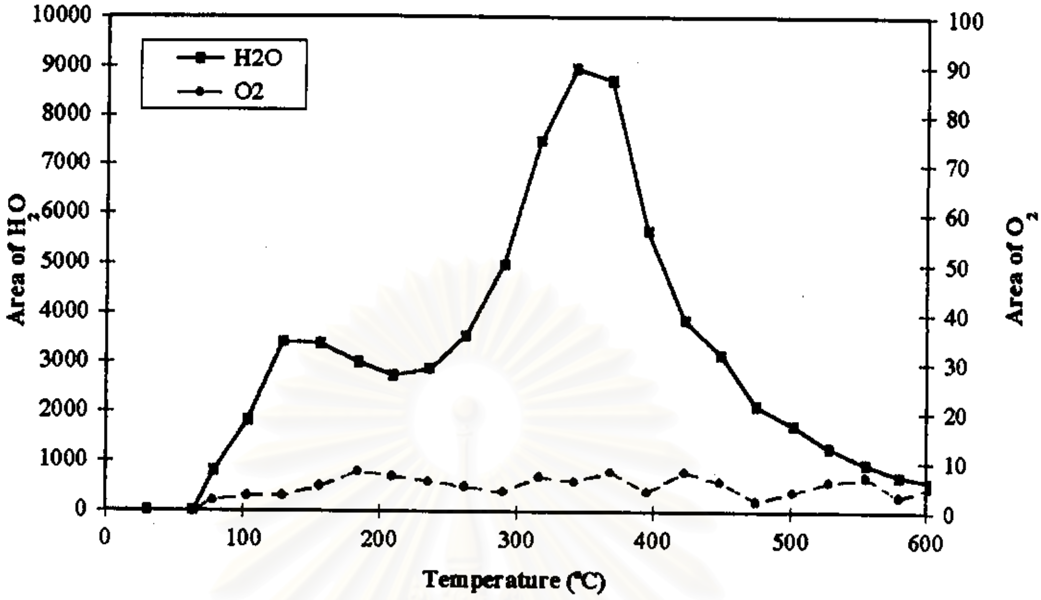

Figure 5.40 Temperature programmed decomposition of 28V-Mg-O (3%Na)

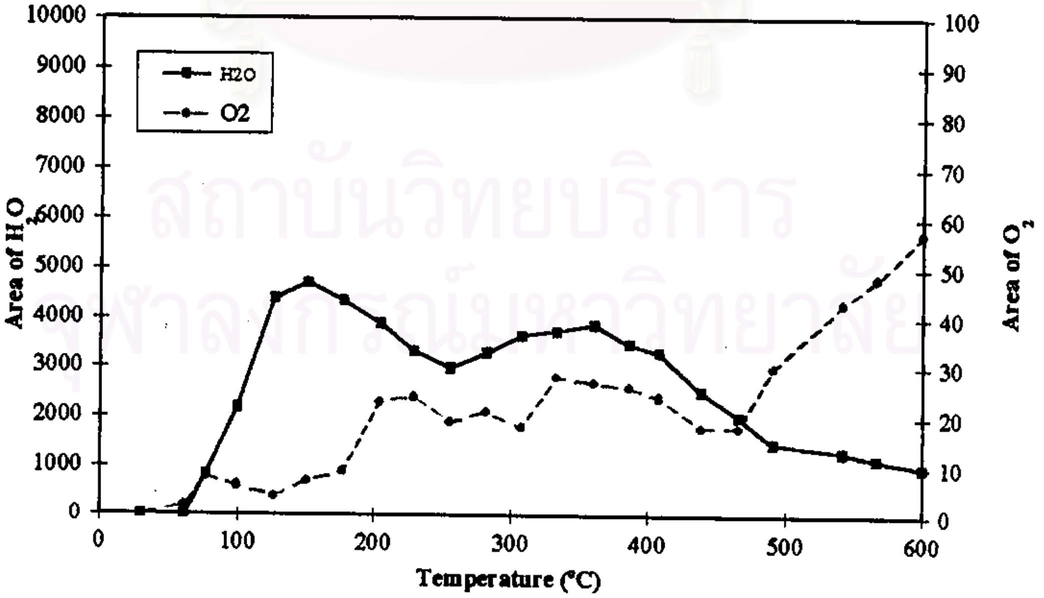

Figure 5.41 Temperature programmed decomposition of 28V-Mg-O (1%K)

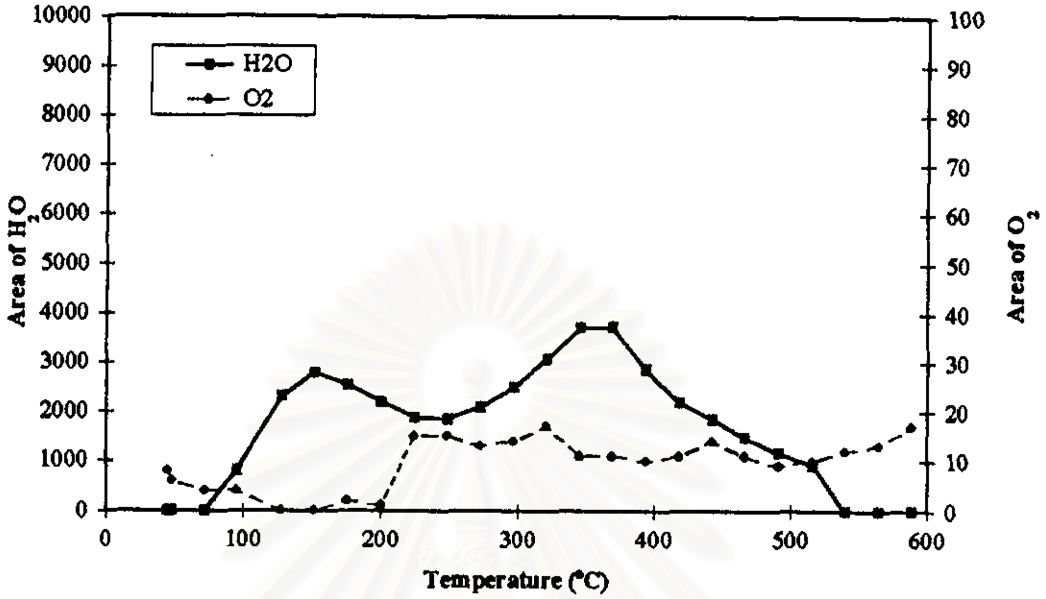

Figure 5.42 Temperature programmed decomposition of 28V-Mg-O (2%K)

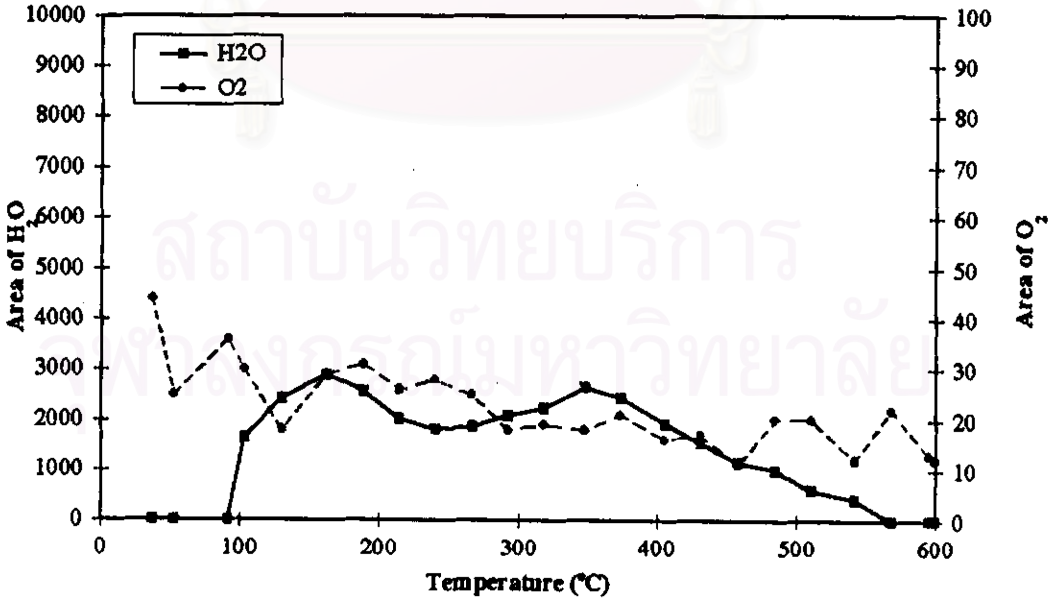

Figure 5.43 Temperature programmed decomposition of 28V-Mg-O (3%K)

5.1.6 CO_2 adsorption

For the oxidative dehydrogenation of propane to propene, the basicity of catalyst is required for inhibiting the combustion reaction of propene. In the nature of V-Mg-O catalyst, there is the acid-base character presented on the catalyst surface. The basicity of V-Mg-O catalyst would support the propene desorption [Pantazidis et al. (1996b)]. However, it is possible that too high basicity may lead to strong adsorption of CO_2, one product in the oxidative dehydrogenation, causing self poisoning of the catalyst.

The CO_2 adsorption is a technique used to measure the basicity of the catalyst. CO_2 adsorption on O^{2-} base sites leads to the formation of carbonate species [Lavalley (1996)]. The outlet gas can be determined by TCD. It is known that the surface of supported vanadium catalysts are usually covered by a layer of adsorbed water [Thammanonkul (1996)]. This water layer inhibits the adsorption of reactant on the catalyst surface, thus, makes the catalyst inactive. This water layer also affects the adsorption of CO_2 on the catalyst surface. Heating the catalyst up to a specific temperature can remove this water layer resulting in the exposure of active sites. This procedure is called pretreatment of catalyst. However, the pretreatment of catalyst can be performed in different atmosphere such as oxidizing or non-oxidizing atmosphere which affects the surface structure of catalyst.

To prepare the pretreated catalyst, the first condition is to keep the catalyst surface in a fully oxidized state by heating the catalyst at 500 °C in air atmosphere for 1 hour. This catalyst will be called V-Mg-O/Air. The second condition which intended to partially reduced the catalyst surface to an extent is similar to the first condition but Ar was used instead of air. This catalyst will be called V-Mg-O/Ar.

Table 5.2 lists the basicity content of all catalyst pretreated in air and Ar. The results are shown in the form of CO_2 mole adsorbed per unit surface area.

From the results of CO_2 adsorption, it can be observed that alkali loaded 28 V-Mg-O has more amount of CO_2 adsorbed than the reference 28 V-Mg-O. The results mean that alkali loading can increase the basicity of the catalyst. When compare all catalyst altogether, the catalyst which has the highest basicity is K loaded 28 V-Mg-O. The order of alkali loading which increases the basicity of catalyst is follows : K>Na>Li. Additionally, the basicity of 28V-Mg-O catalyst increases with increasing the amount of alkali loading. In the case of Li, the different of the amount of CO_2 adsorbed content between 1 wt.%Li and 2 wt.%Li equals to 0.73, between 2 wt.%Li and 3 wt.%Li equals to 6.49. It can be noted that the content of CO_2 adsorbed in Li loaded 28V-Mg-O increases rapidly in the range of 2 wt.% to 3 wt.%, possibly due to the formation of alkali oxide phase in the catalyst structure. The phenomena of Na and K loaded 28V-Mg-O are similar to that of Li loaded 28V-Mg-O. The rapid increase of CO_2 adsorbed content in both Na and K loaded 28V-Mg-O occurs in the range of 1wt.% alkali to 2 wt.% alkali. Conclusionly, the more the basicity of alkali, the further the formation of alkali oxide phase in the catalyst structure.

Table 5.2 The basicity content of catalysts pretreated in Ar and Air

catalysts	pretreatment in Ar $\mu mol\ CO_2 / m.^2$	pretreatment in Air $\mu mol\ CO_2 / m.^2$
28V-Mg-O	5.10	4.80
28V-Mg-O(1%Li)	4.90	4.60
28V-Mg-O(2%Li)	5.99	5.47
28V-Mg-O(3%Li)	16.35	12.96
28V-Mg-O(1%Na)	6.14	5.24
28V-Mg-O(2%Na)	19.10	10.47
28V-Mg-O(3%Na)	22.69	13.14
28V-Mg-O(1%K)	6.41	5.64
28V-Mg-O(2%K)	23.48	21.40
28V-Mg-O(3%K)	32.09	31.50

For each catalysts pretreated in Ar and air, it can be seen that catalyst pretreatment in Ar has higher basicity than that one pretreated in air. It can be explained that the catalyst pretreated in Ar at the specific temperature will be converted to a reduced form. Thus, after a catalyst is pretreated in Ar, it will have more basicity.

5.2 Catalytic reaction

In this section, the catalytic property of the V-Mg-O catalysts which are pretreated in different atmosphere is investigated by using the oxidative dehydrogenation reaction of propane to propene as test reaction.

5.2.1 Catalysts pretreated in air

The catalytic property of the 28 V-Mg-O/Air catalyst is presented in figure 5.44. At low reaction temperatures, the activity of 28 V-Mg-O/Air increases slightly from 4% to 10% with increasing temperature from 300°C to 400°C . When the reaction temperature is higher than 400 ° C , the activity increases rapidly up to 99% at 600 ° C , while the selectivity to propene gradually decreases to nearly zero at 550 °C . At the high reaction temperature, the propene as ODH product may react further with oxygen to combustion products such as CO, CO_2 and H_2O. This is the cause of the decreasing of the propene selectivity to almost zero at high reaction temperature.

Figures 5.45 to 5.47 exhibit the effect of Li loading on the performance of 28 V-Mg-O catalyst. For 28 V-Mg-O (1%Li)/Air. It can be seen that in the initial reaction temperature (300-400°C), the propane conversion is quite low for all Li loaded catalyst. At the temperature higher than 400°C , C_3H_8 conversion gradually increases with increasing the temperature of experiment. However, at the reaction temperature between 300°C and 600°C, the propene selectivity is quite constant and very low. In addition, when the amount of loading Li is increased, the propene selectivity and the activity are also increased. From figures 5.46 and 5.47, the absence of both selectivity and yield curve at the reaction temperature between 300-350°C is because both selectivity and yield are not defined because of zero conversion at 300 °C. Conclusionly, the more the amount of Li, the more the both of selectivity and the activity. To compare with 28 V-Mg-O/ Air, it can be observed that when loading Li into 28 V-Mg-O, the selectivity to propene is increased, but the activity of catalyst is declined.

The results of the Na loading in 28 V-Mg-O are shown in figures 5.48 to 5.50 For 28 V-Mg-O(1%Na)/Air, it can be seen that the activity is similar to that of 28 V-Mg-O(1%Li)/Air. Figure 5.49 shows the different ability of 28 V-Mg-O (2%Na) /Air. It is found that 28 V-Mg-O (2%Na)/Air had more reactivity than 28 V-Mg-O (1%Na)/Air. For 28V-Mg-O (2%Na), the propane conversion increases rapidly to a maximum conversion at 62% at 500°C . After that, the conversion of propane decreases again to be about 45% at 600°C. However, the selectivity to propene is quite constant and very low. 28 V-Mg-O(3%Na)/Air has the same trend as 28 V-Mg-O (2%Na) /Air, expect the activity of 28 V-Mg-O (3%Na)/Air is higher. Thus, the activity of catalyst increases with increasing the amount of Na. However, the increasing amount of Na has no effect on the propene selectivity.

In the same condition with the above mentioned catalysts, the results of 28 V-Mg-O loaded with potassium are exhibited in figures 5.51 to 5.53. For 28 V-Mg-O (1%K)/Air, figure 5.51, the activity shows the same trend as that of 28 V-Mg-O (1%Li)/Air which increases slightly with temperature, while the selectivity to propene shows a slight decrease. However, the effect of adding K in 28 V-Mg-O on the catalytic performance is different from the other. The activity of the catalyst decreases with increasing amount of K, while the propene selectivity increases insignificantly. To compare with 28 V-Mg-O/Air, it can be seen that the activity of catalyst dropped rapidly when K is loaded into 28 V-Mg-O, but the propene selectivity is almost the same.

From the above results , it may be concluded that loading a small amount of alkali metals in 28 V-Mg-O may disturb the adsorption of propane on the catalyst surface, which makes the activity of catalyst decreases. From the TPD results, it can be found that 28 V-Mg-O with the small amount of alkali can be reduced easily . When the alkali content increases, the catalyst surface can be less reduced. The less the reducibility of catalyst surface, the more the dominant propene selectivity. [29,88]. Thus, Li loading in 28 V-Mg-O increases the propene selectivity, but is different from Na and K loading.

In the case of Na loading , it is found that the propene selectivity is quite constant and very low, while the activity of the catalyst increases rapidly. It is possible that when the catalyst is pretreated in oxidizing atmosphere, the catalyst structure can be oxidized to be a stable structure which prefer to the oxidation of propene.

In the case of K loading, loading too high amount of K does not improve both the propene selectivity and activity of catalyst. Kung and colleagues (1996a) reported that the presence of residual potassium in the oxide lowered the propene selectivity, due to it increased the thermal stability of magnesium pyrovanadate against reaction with MgO to form magnesium orthovanadate. Besides, refer to CO_2 adsorption , alkali loading increases the basicity of catalyst . K loading may increase the basicity of catalyst enough to support the adsorption of CO_2 , by product, on the catalyst surface, causing inhibition of the ODH reaction.

It can be concluded that alkali metals (Li, Na and K) loading in 28 V-Mg-O/Air affects the activity of 28 V-Mg-O /Air which is decreased at the high reaction temperature. Besides, among all of 28V-Mg-O/Air which are loaded with alkali metals ,only Li loading can improve the propene selectivity. Loading a proper amount of alkali metals can increase the basicity of catalyst to a suitable extent for supporting the propene desorption.

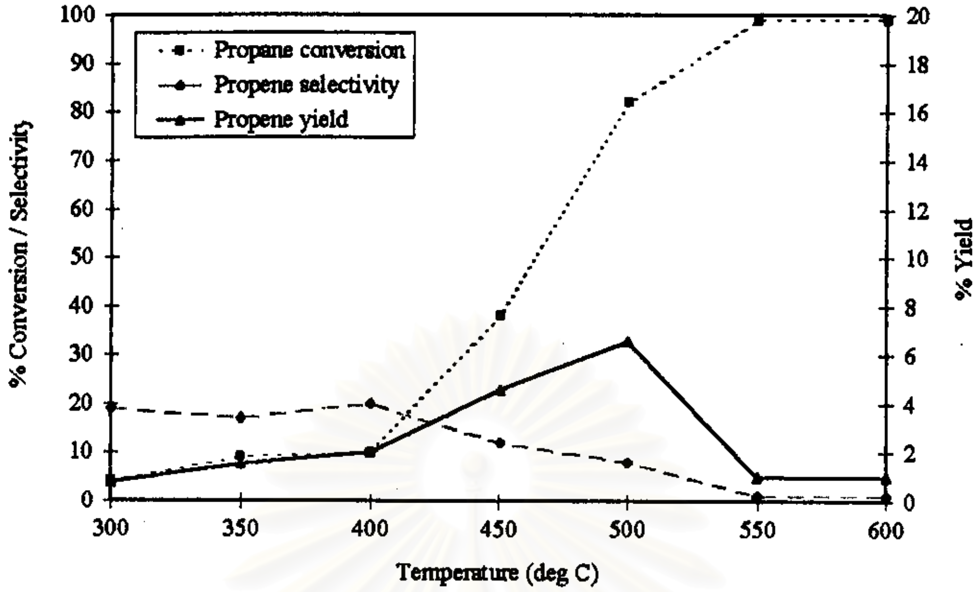

Figure 5.44 The catalytic properties of 28V-Mg-O/Air in the oxidative dehydrogenation of propane to propene.

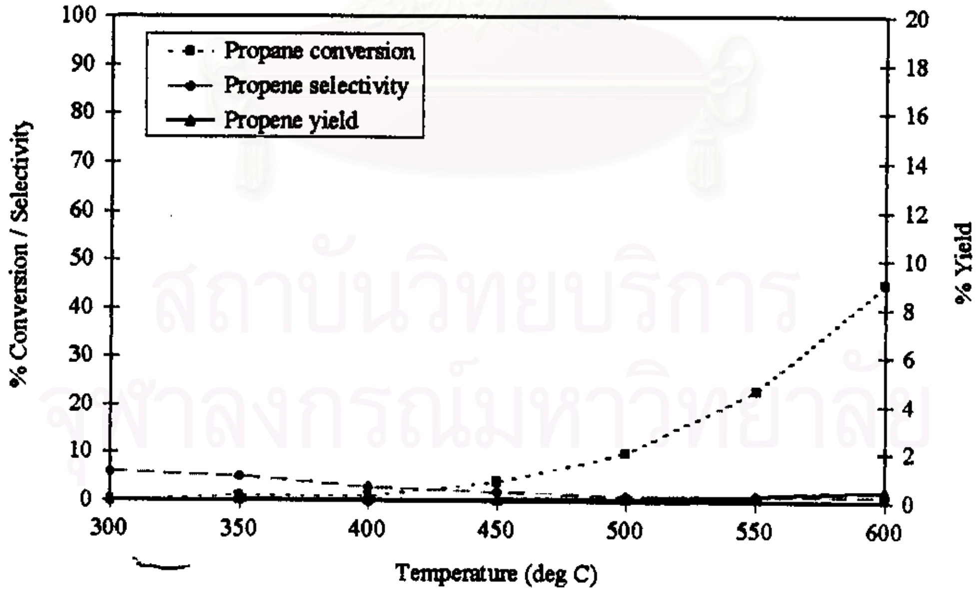

Figure 5.45 The catalytic properties of 28V-Mg-O (1%Li)/Air in the oxidative dehydrogenation of propane to propene.

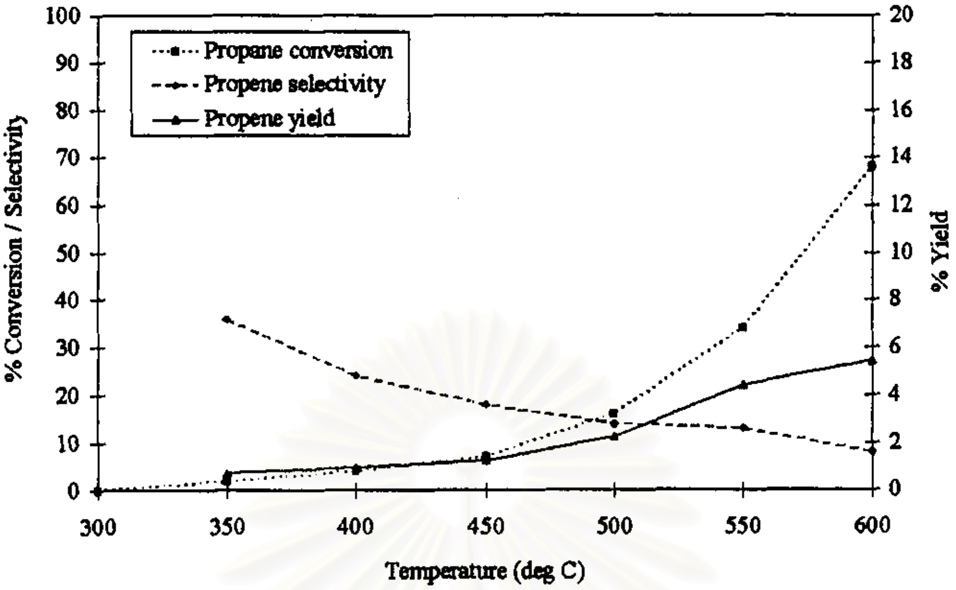

Figure 5.46 The catalytic properties of 28V-Mg-O (2%Li)/Air in the oxidative dehydrogenation of propane to propene.

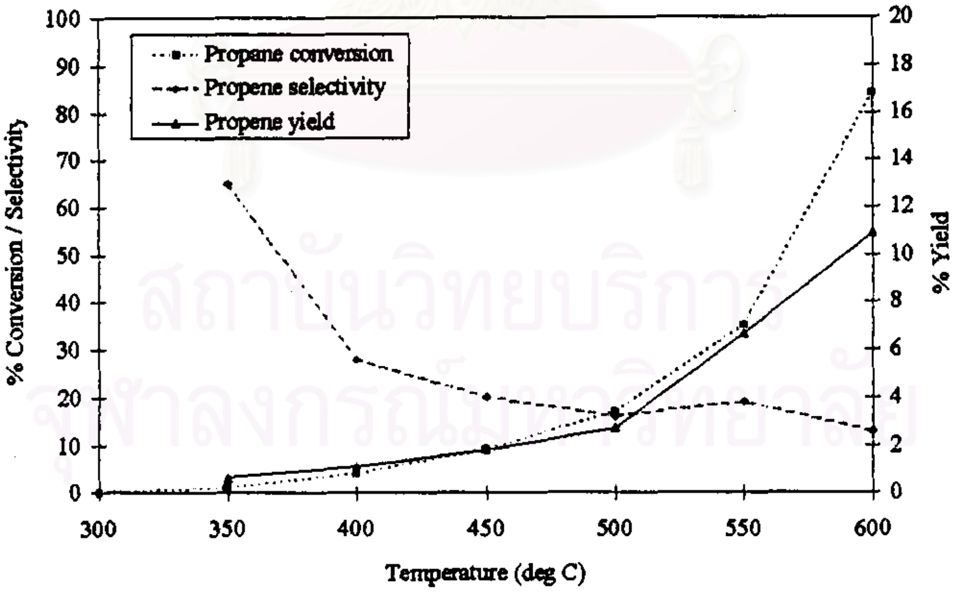

Figure 5.47 The catalytic properties of 28V-Mg-O (3%Li)/Air in the oxidative dehydrogenation of propane to propene.

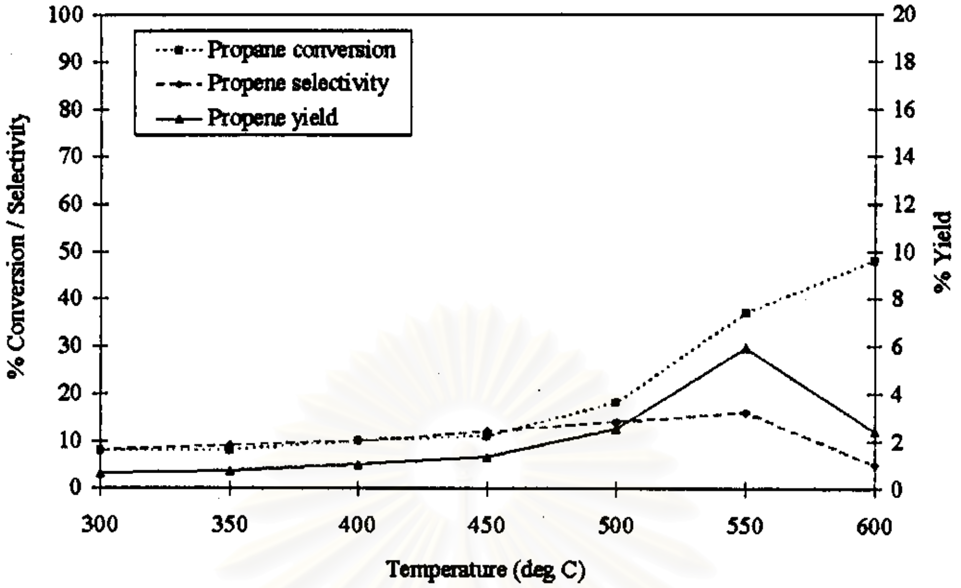

Figure 5.48 The catalytic properties of 28V-Mg-O (1%Na)/Air in the oxidative dehydrogenation of propane to propene.

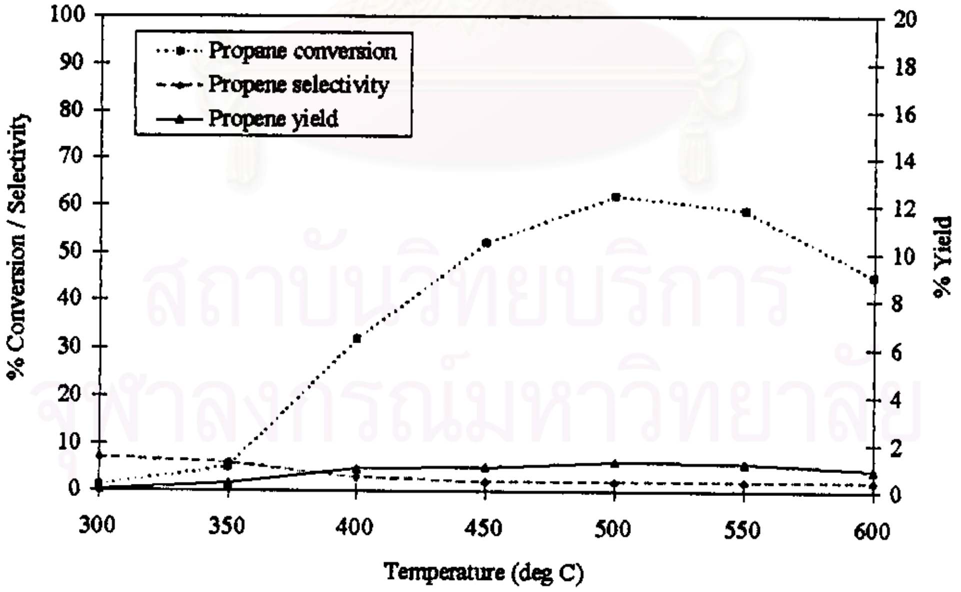

Figure 5.49 The catalytic properties of 28V-Mg-O (2%Na)/Air in the oxidative dehydrogenation of propane to propene.

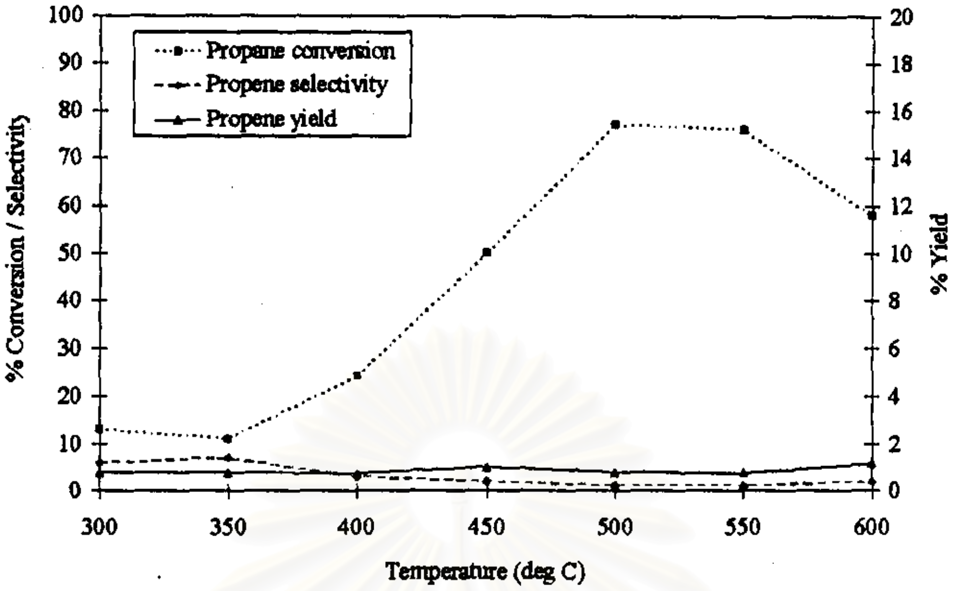

Figure 5.50 The catalytic properties of 28 V-Mg-O (3%Na)/Air in the oxidative dehydrogenation of propane to propene.

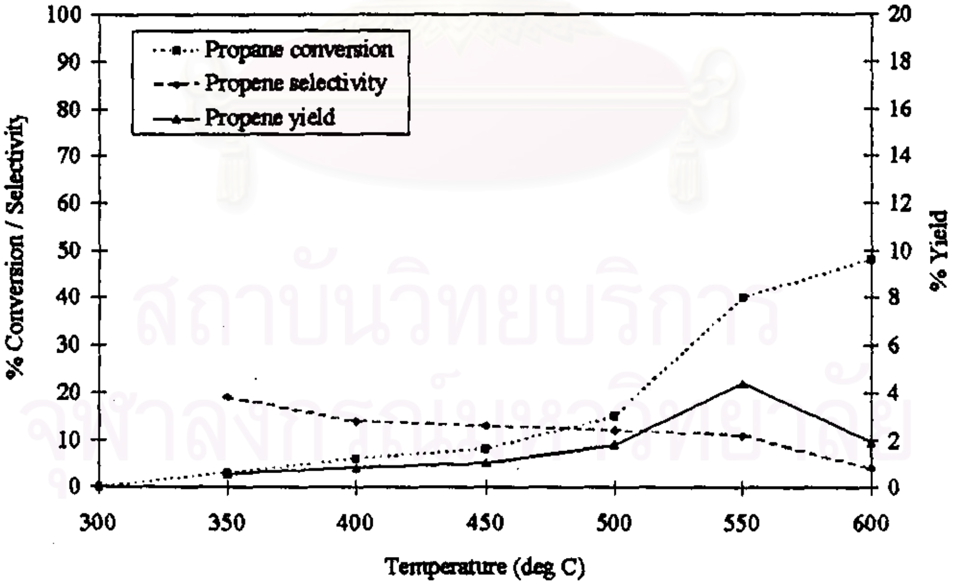

Figure 5.51 The catalytic properties of 28V-Mg-O (1%K)/Air in the oxidative dehydrogenation of propane to propene.

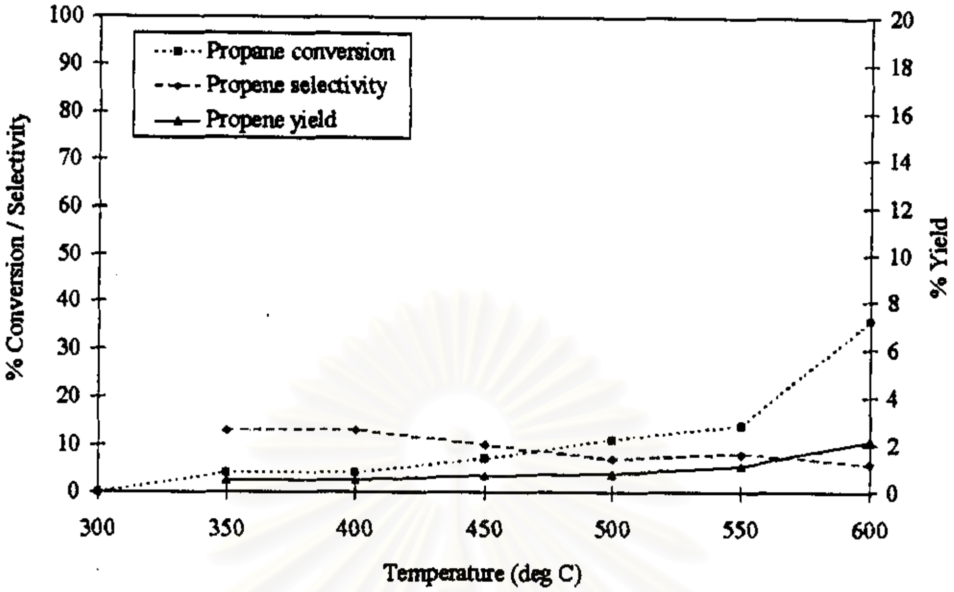

Figure 5.52 The catalytic properties of 28 V-Mg-O (2%K)/Air in the oxidative dehydrogenation of propane to propene.

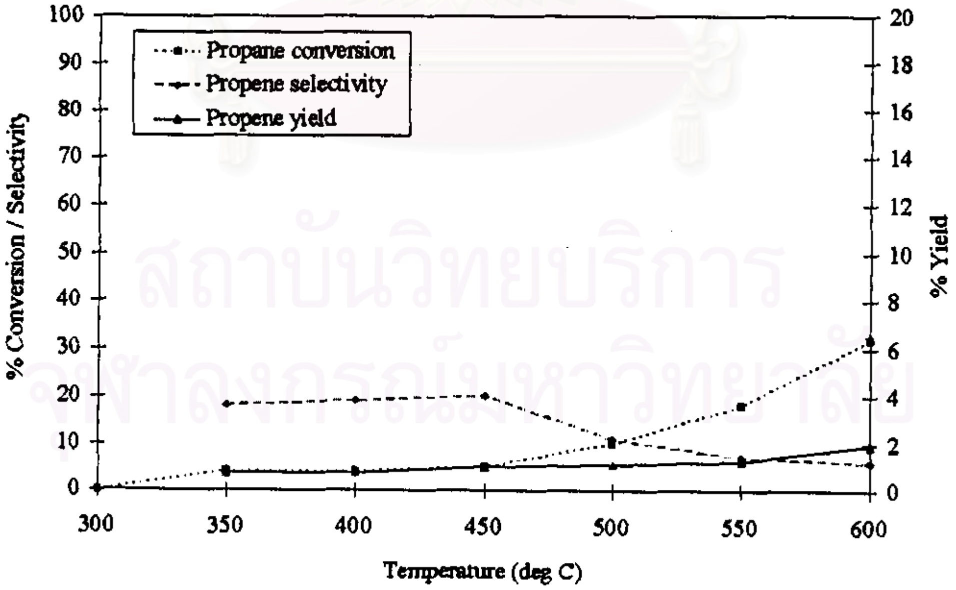

Figure 5.53 The catalytic properties of 28V-Mg-O (3%K)/Air in the oxidative dehydrogenation of propane to propene.

5.2.2 Catalysts pretreated in Ar

Figure 5.54 shows the activity and selectivity of 28 V-Mg-O/Ar. The figure demonstrates that the activity of 28 V-Mg-O/Ar is similar to that of 28V-Mg-O/Air. The activity increases slowly in the beginning (300-450°C) and increases very rapidly up to 99% at 550°C. In the temperature range of 300-350°C, the propene selectivity is relatively constant about 51%. Then it rapidly decreases to nearly zero at 550°C.

Figures 5.55 to 5.57 illustrate the effect of Li loading into 28 V-Mg-O/Ar on the catalytic property. For 28 V-Mg-O(1%Li)/Ar (figure 5.55) in the reaction temperature range of 350-600°C , the activity increases steadily up to 65%, while the propene selectivity is not quite constant. When Li loading is increased up to 2% and 3% as presented in figures 5.56 and 5.57, respectively , one can see that the activity increases more rapidly with increasing the reaction temperature, but the propene selectivity decreases rapidly nearly to zero at 600°C. In addition, the more the Li loading in 28 V-Mg-O, the more the both of activity and the propene selectivity, which is similar to the results of catalyst pretreated in air. To compare with 28 V-Mg-O/Ar, adding Li improve the propene selectivity, while the activity of catalyst decreases.

The activity and selectivity of Na loaded 28V-Mg-O /Ar catalyst are presented in figures 5.58 to 5.60. For 28V-Mg-O (1%Na) / Ar , the propane conversion increases gradually in the reaction temperature range 300-600°C, while the propene selectivity is in the wave form. Besides, the propene selectivity increases with increasing the amount of loaded Na, which is different from the activity. The activity of the catalyst declines with increasing the amount of loaded Na. To compare with 28 V-Mg-O/Ar, it can be observed that Na loading in 28 V-Mg-O/Ar will enhance the propene selectivity, but decrease the activity of catalyst.

In the last case, effects of K loading on 28 V-Mg-O are shown in figures 5.61 to 5.63. Potassium also exhibits some effects on the catalytic property. In the same reaction condition, 28V-Mg-O(1%K)/Ar shows the decrease of the propene selectivity with increasing the reaction temperature, while the activity of the catalyst rapidly increases up to 98% at 600°C. When the amount of K loading is increased, the propene selectivity also increases . To compare with 28 V-Mg-O/Ar , it can be seen that loading K in 28 V-Mg-O/Ar will increase the propene selectivity.

Conclusionly, alkali metal loading in 28 V-Mg-O/Ar can improve the propene selectivity ,with the expense of the activity of the catalyst.

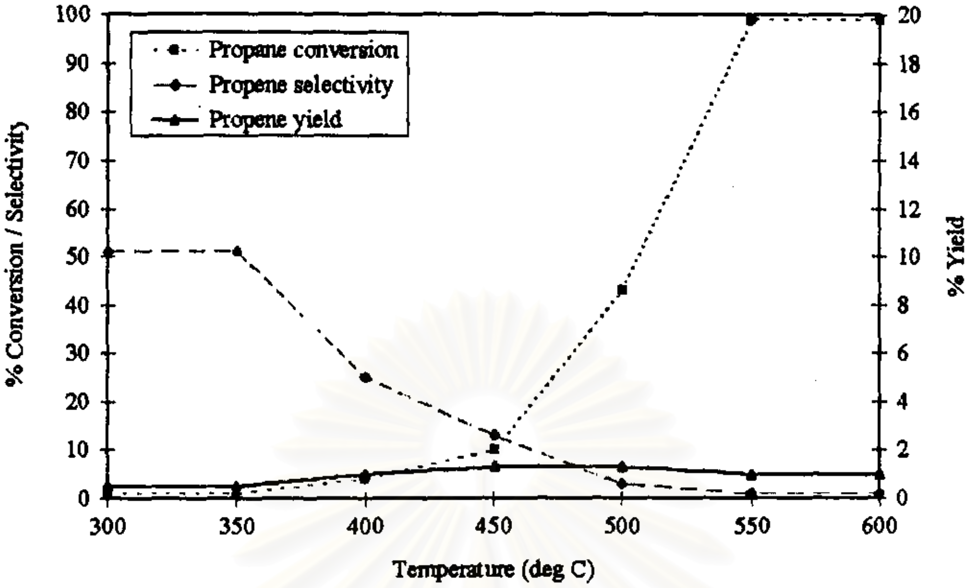

Figure 5.54 The catalytic properties of 28V-Mg-O / Ar in the oxidative dehydrogenation of propane to propene.

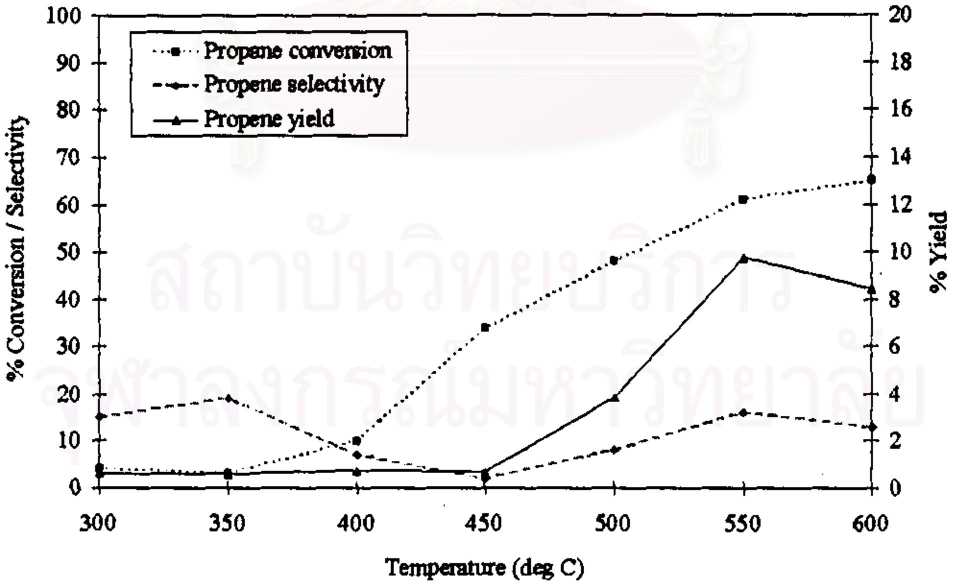

Figure 5.55 The catalytic properties of 28V-Mg-O (1%Li)/Ar in the oxidative dehydrogenation of propane to propene.

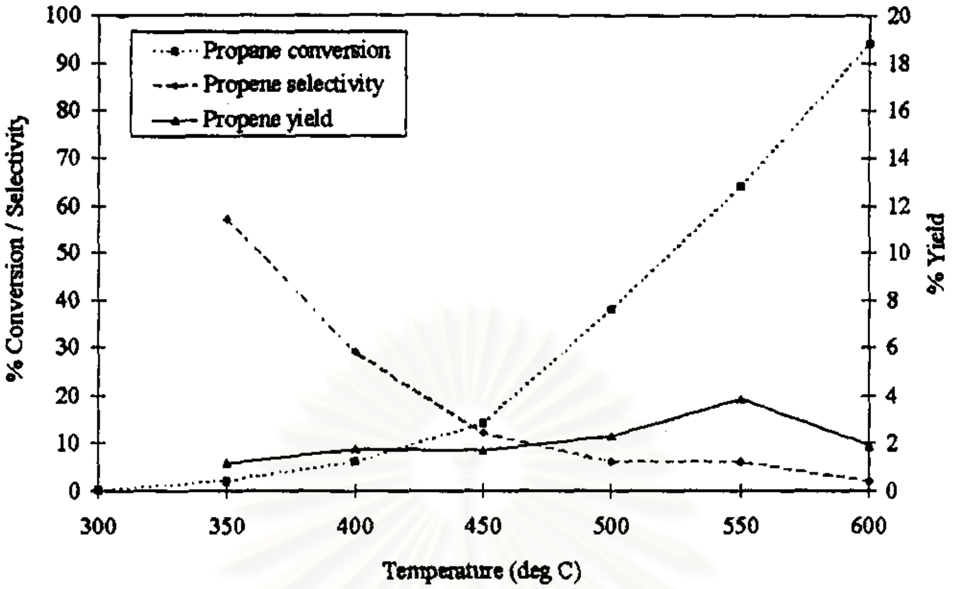

Figure 5.56 The catalytic properties of 28V-Mg-O (2%Li)/Ar in the oxidative dehydrogenation of propane to propene.

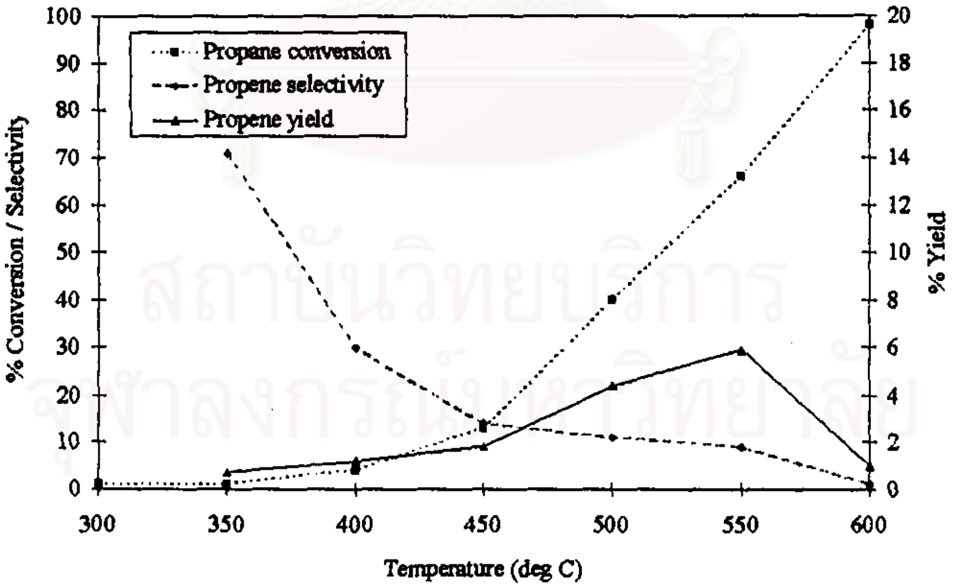

Figure 5.57 The catalytic properties of 28V-Mg-O (3%Li)/Ar in the oxidative dehydrogenation of propane to propene.

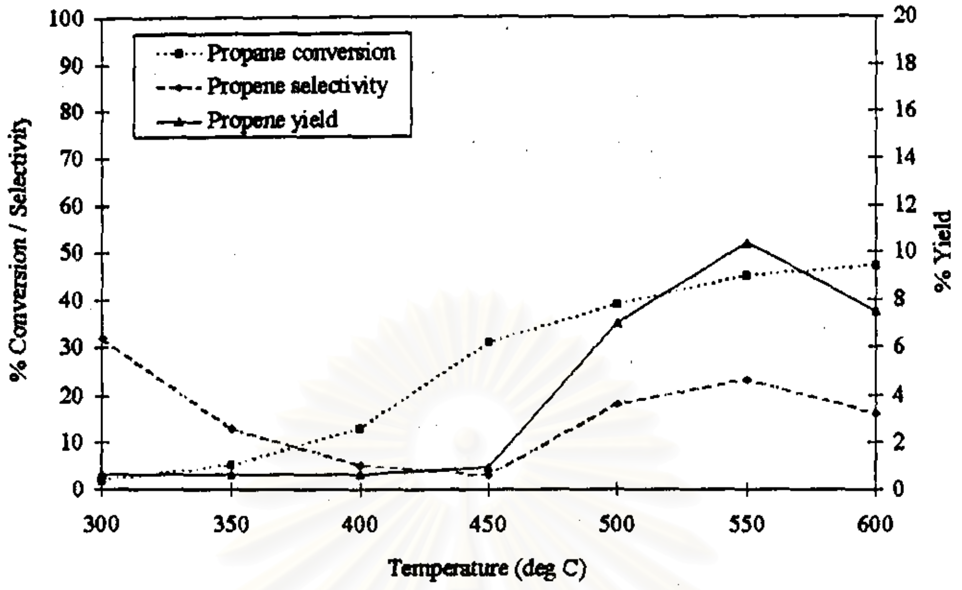

Figure 5.58 The catalytic properties of 28V-Mg-O (1%Na)/Ar in the oxidative dehydrogenation of propane to propene.

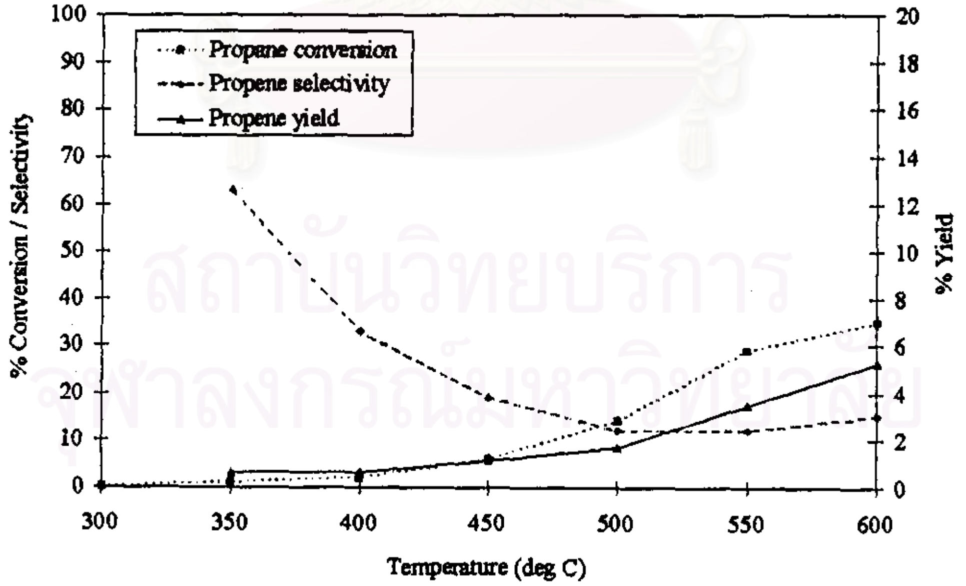

Figure 5.59 The catalytic properties of 28V-Mg-O (2%Na)/Ar in the oxidative dehydrogenation of propane to propene.

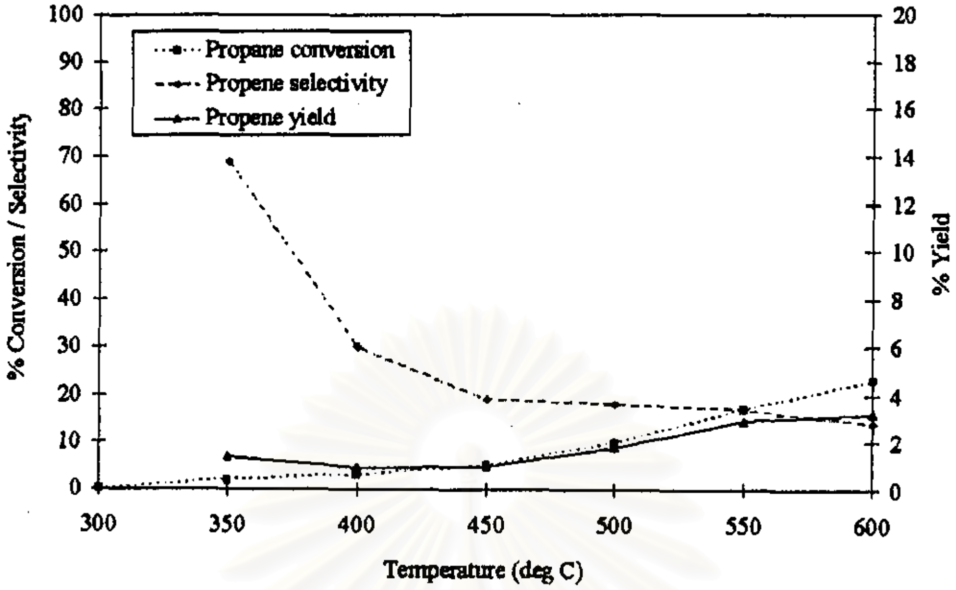

Figure 5.60 The catalytic properties of 28V-Mg-O (3%Na)/Ar in the oxidative dehydrogenation of propane to propene.

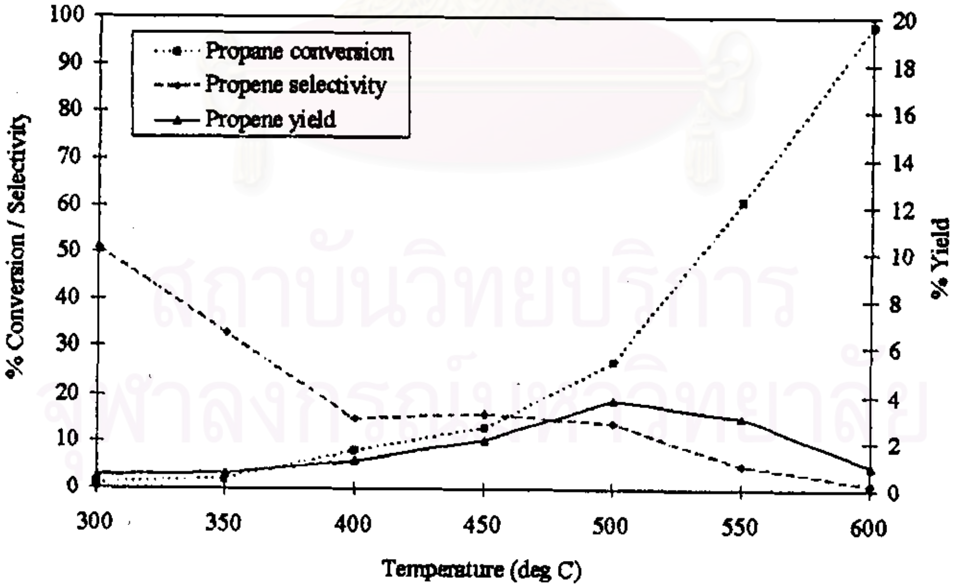

Figure 5.61 The catalytic properties of 28V-Mg-O (1%K)/Ar in the oxidative dehydrogenation of propane to propene.

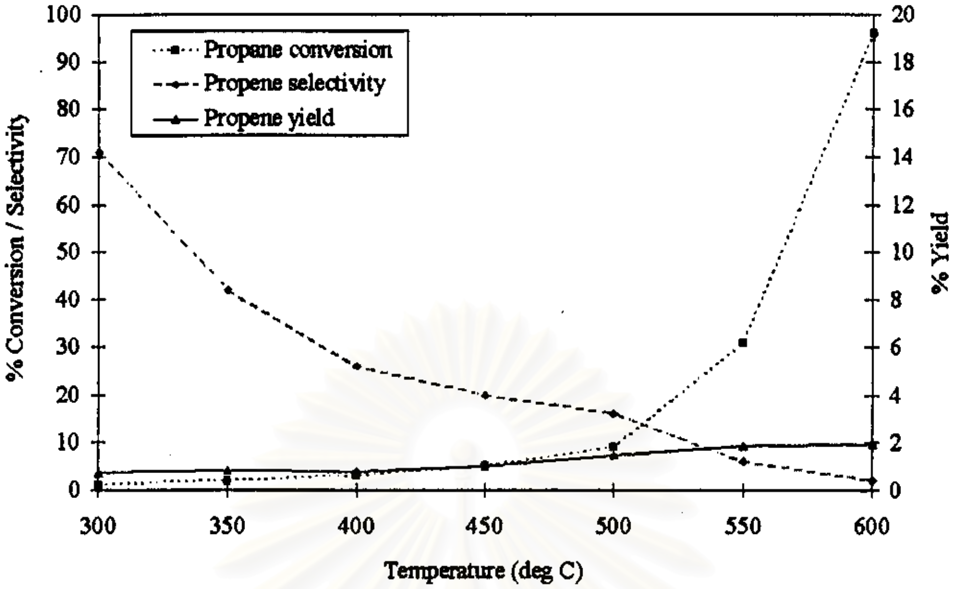

Figure 5.62 The catalytic properties of 28V-Mg-O (2%K)/Ar in the oxidative dehydrogenation of propane to propene.

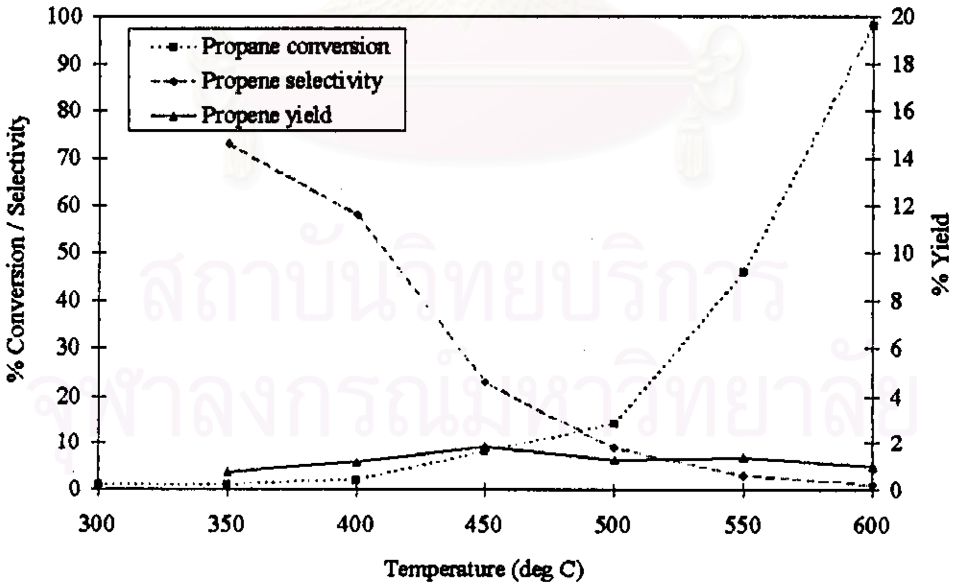

Figure 5.63 The catalytic properties of 28V-Mg-O (3%K)/Ar in the oxidative dehydrogenation of propane to propene.

5.2.3 Comparison between catalyst pretreated with Air and Ar

The reaction study shows that both 28 V-Mg-O/Ar and 28 V-Mg-O/Air exhibit the same propane conversions but different propene selectivity. Propene selectivity of 28 V-Mg-O/Ar is about two times higher in the reaction temperature region below 500°C. From the result of CO_2 adsorption 28 V-Mg-O/Ar is more basicity than 28 V-Mg-O/Air, due to reduced species formed on the structure of 28 V-Mg-O/Ar. It is possible that in the temperature region below 500°C, the basicity of 28 V-Mg-O/Ar improves the propene selectivity and the gas phase oxygen in feed gas may not be effective enough in the reoxidation of the catalyst surface. However, in the temperature higher than 500 °C the gaseous oxygen can oxidize the reduced surface of the 28 V-Mg-O/Ar catalyst back to its oxidized form, the same form as of the 28 V-Mg-O/Air . Therefore, both catalysts have the same surface structure and the the same catalytic properties.

Considering of Li loading, catalyst pretreated in Ar has more propene selectivity and activity than that pretreated in air. It can also be described by the above reasons. The catalyst surface reduced in Ar atmosphere will become more basicity, that is an inhibitor for the combustion of propene. Furthermore, the more basicity of the catalyst which is pretreated in Ar may also prefer the oxidation of propane on the basic surface of catalyst.

For Na loading, it can be found that propene selectivity of catalyst in Ar is higher , while the conversion is lower than that in Air. For the catalyst pretreated in Air, the propene selectivity is quite constant and very low, but activity increased. That means the pretreatment of catalyst under oxidizing atmosphere will change the catalyst structure to the oxidized form which prefers to the combustion reacton.

In the case of K loading, the presence of potassium in the oxide catalyst lowered the propene selectivity [Kung et al. (1992)]. However, the more basicity of catalyst pretreated in Ar atmosphere will support the activity and propene selectivity

to be better. Thus, the catalyst pretreated in air provides worse the catalytic properties than the catalyst pretreated in Ar

5.2.4 Dynamic behaviour of V-Mg-O catalyst

Figures 5.66 to 5.69 exhibit the catalytic properties of 28V-Mg-O which pretreated in different atmosphere in the same reaction condition. Firstly, the catalyst which pretreated in air is used in the ODH reaction (figure 5.66) . After that that same catalyst is pretreated again in Ar atmosphere for 1 hour at 500°C (figure 5.67), which used in the same ODH reaction. The experiment is repeated again for determining the reoxidation of catalyst. When the catalytic reaction is repeated after a continuous run, the activity of 28V-Mg-O in all cases (figure 5.66 to 5.69) is nearly to 70% at the reaction temperature 600°C, while the propene selectivity is quite constant and low. For the repeated run of 28V-Mg-O/Air (figure 5.68) and 28V-Mg-O/Ar (figure 5.69),within the reaction temperature range 300-600 °C, it can be seen that the activity decrease significantly. It is possible that the catalyst which is pretreated in a non-oxidized atmosphere can be reduced to form a new structure, which is not reversible to be the oxidizes one.

Figures 5.70 to 5.73 illustrate the catalytic properties of Na loaded in 28 V-Mg-O which was treated in the different atmosphere in the same reaction condition. The result of Na loaded in 28V-Mg-O is similar to that of 28V-Mg-O, but more significant. Therefore, alkali loaded catalysts when pretreated in Ar cannot be reoxidized to be the oxidized form permanently.

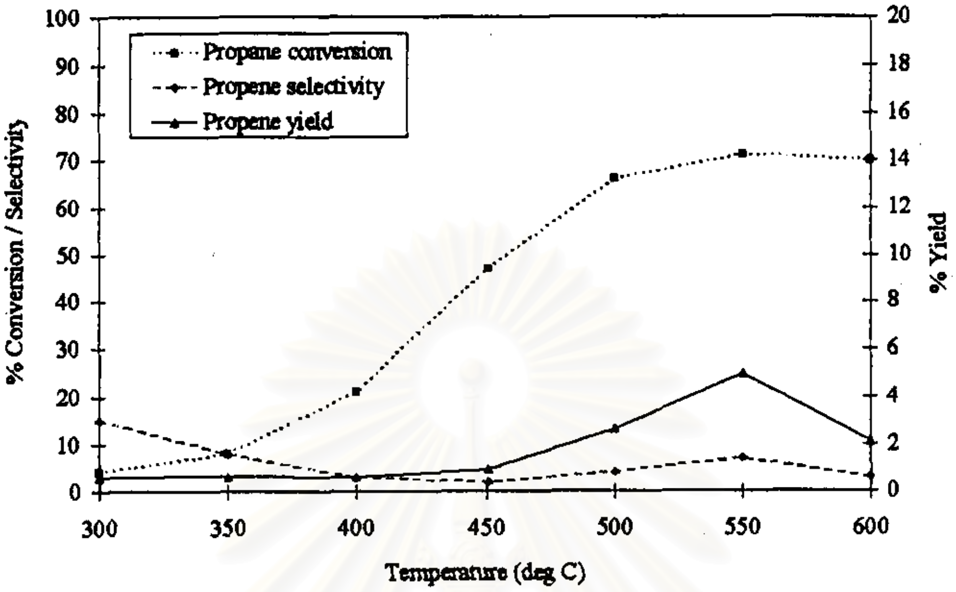

Figure 5.64 The catalytic properties of 28V-Mg-O/Air in the oxidative dehydrogenation of propane to propene.

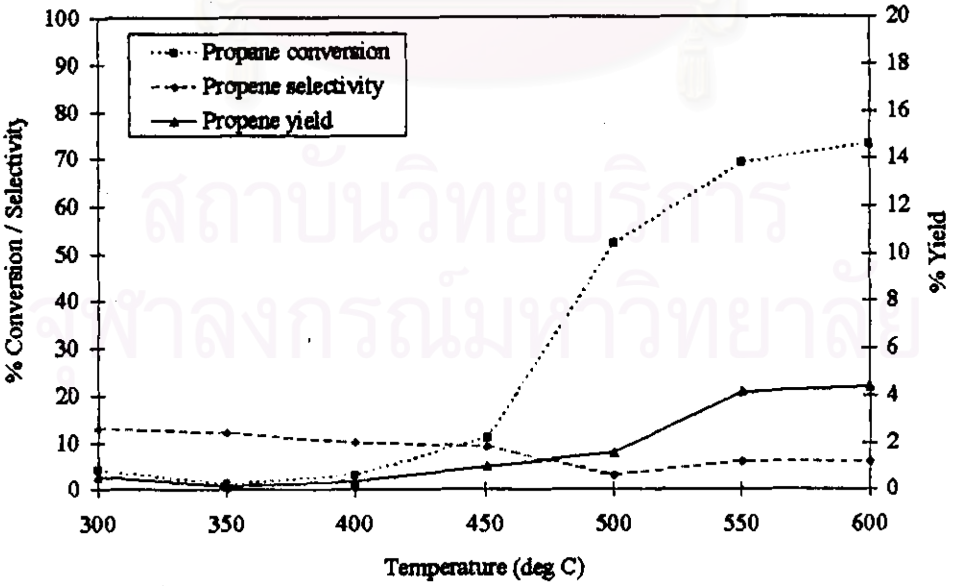

Figure 5.65 The catalytic properties of 28V-Mg-O/Ar in the oxidative dehydrogenation of propane to propene.

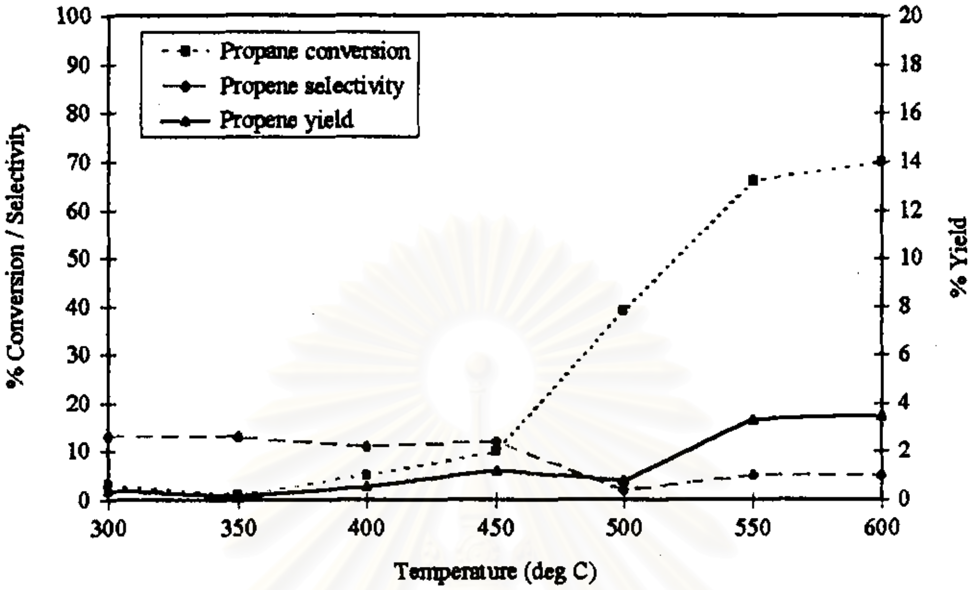

Figure 5.66 The catalytic properties of repeated run over 28V-Mg-O/Air in the oxidative dehydrogenation of propane to propene.

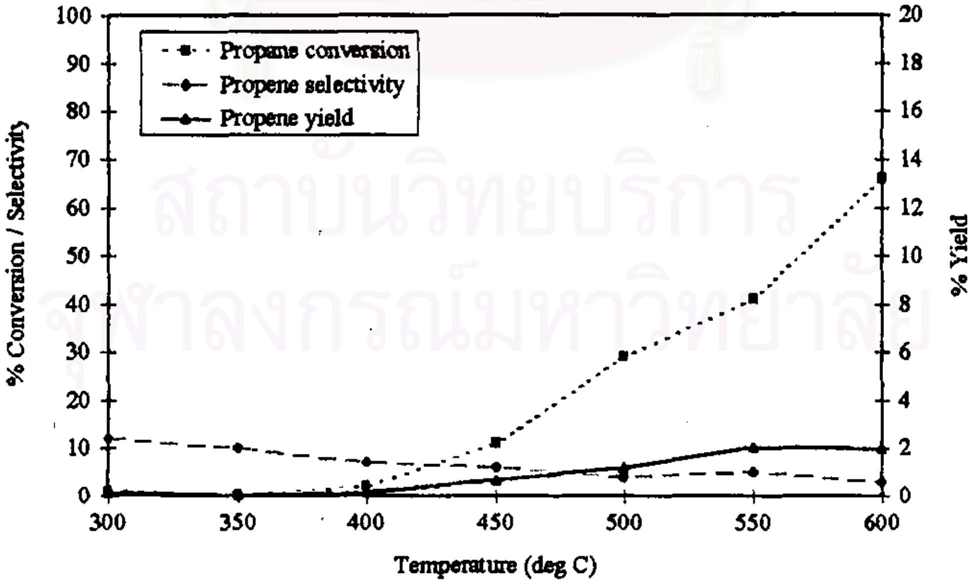

Figure 5.67 The catalytic properties of repeated run over 28V-Mg-O/Ar in the oxidative dehydrogenation of propane to propene.

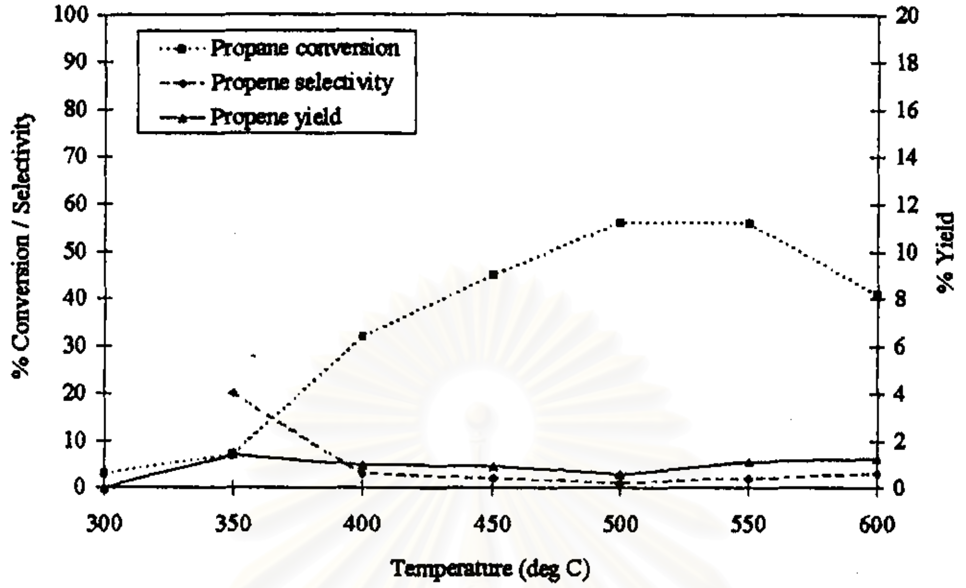

Figure 5.68 The catalytic properties of 28V-Mg-O (2%Na)/Air in the oxidative dehydrogenation of propane to propene.

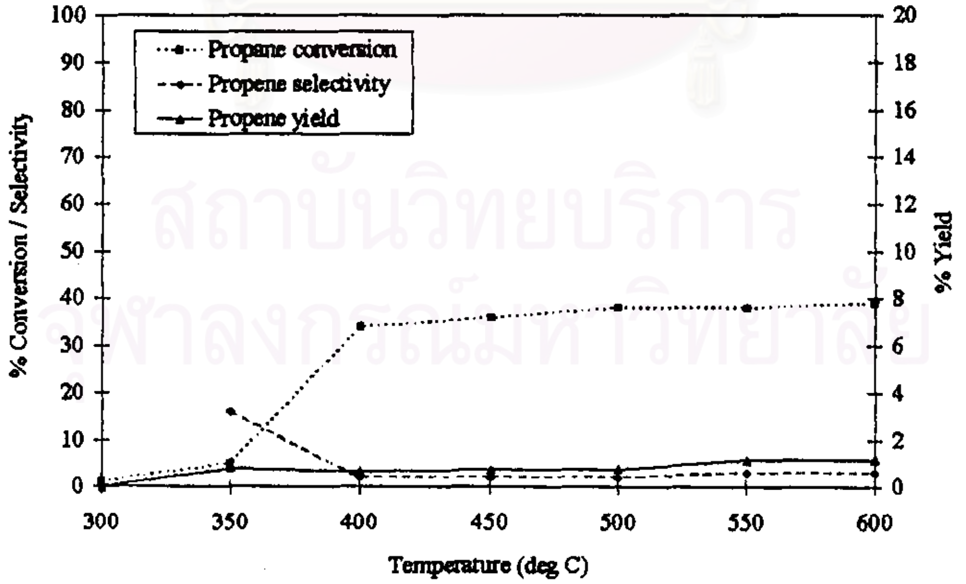

Figure 5.69 The catalytic properties of 28V-Mg-O (2%Na)/Ar in the oxidative dehydrogenation of propane to propene.

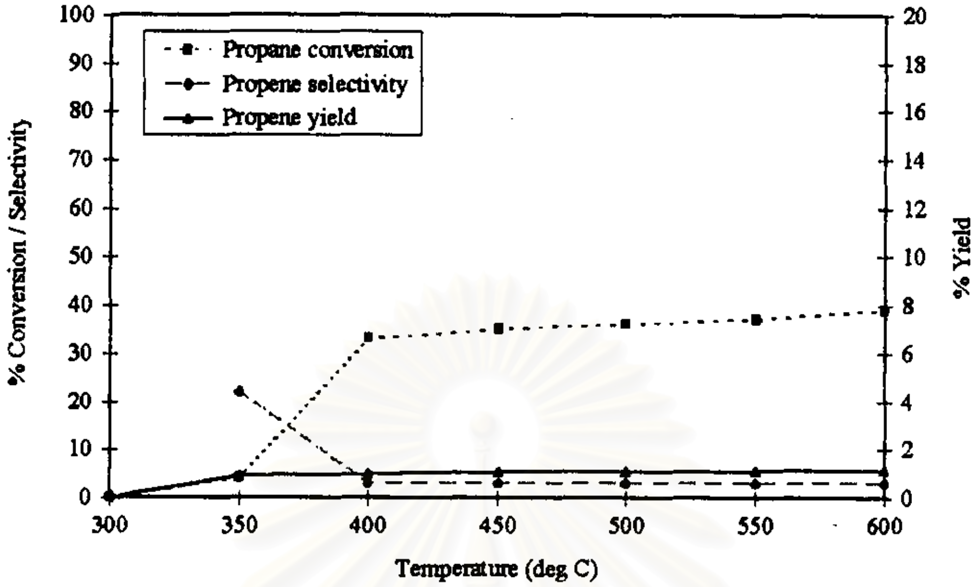

Figure 5.70 The catalytic properties of repeated run over 28V-Mg-O (2%Na)/Air in the oxidative dehydrogenation of propane to propene.

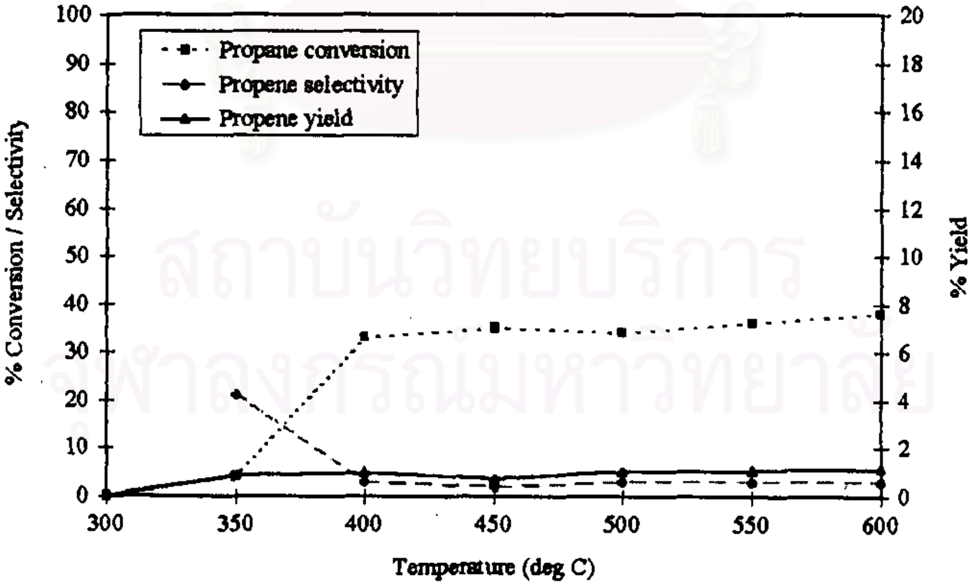

Figure 5.71 The catalytic properties of repeated run over 28V-Mg-O (2%Na)/Ar in the oxidative dehydrogenation of propane to propene.

5.2.5 Catalytic properties of V-Mg-O layer

Refer to the XRD results, the structure of all 28V-Mg-O catalysts is similar to that of MgO. This means that vanadium may form some phases which cannot be detected by XRD technique, i.e. small crystal and/or amorphous phase. When the catalysts were analyzed by FT-IR, some V-Mg-O compounds can be observed. This means that there is a thin layer of some V-Mg-O compounds distributed on the surface of 28V-Mg-O. This thin layer of V-Mg-O compound comprises of V-O-V species and VO_3 species as the active sites of 28 V-Mg-O in the oxidative dehydrogenation. After alkali metal loading in 28 V-Mg-O, the alkali metal affects the active sites on the V-Mg-O layer, especially V-O-V species. The alkali metal may form V-O-M and/or M-O-M structure on the catalyst surface apart from V-O-V species, where M is alkali metal. Besides, for all of 28 V-Mg-O catalysts investigated, the presence of V_2O_5 which provides the oxygenate products is not observed on the catalyst structure.

When heating the catalyst in the condition of TGA experiment, it was observed that some species lost from the catalyst structure. From TPD experiment, H_2O is found to be the main species lost from the catalysts accompanied with a small amount of O_2.

For the oxidative dehydrogenation of propane, it is known that the basicity of catalyst is required for inhibiting the consecutive reaction of propene. The results of CO_2 adsorption confirmed that the alkali loading can increase the basicity of catalyst. The more the alkali content, the more the basicity of catalyst.

The catalytic performance of V-Mg-O catalysts pretreated in the different atmosphere is investigated by using the oxidative dehydrogenation of propane to propene. It is found that the activity of 28V-Mg-O /Ar is the same as that of 28V-Mg-O/Air but different propene selectivity which is twice higher in the temperature below 500°C. From the IR results (see published paper in appendix E) , the IR spectrum of 28V-Mg-O/Air shows clearer shoulder at 660 cm^{-1} of V-O-V species than the spectrum of 28V-Mg-O/Ar. This means that the treatment of 28 V-Mg-O in Ar caused some loss of oxygen from V-O-V species, resulted in lower V-O-V species concentration on the surface of 28 V-Mg-O/Ar than on the surface of 28V-Mg-O/Air. According to our previous published paper (appendix E), it has been shown that the VO_3 structure acts as propane activation and the V-O-V structure involves in the propene selectivity. Hence, the pretreatment of 28V-Mg-O in non-oxidizing atmosphere, Ar, can improve the propene selectivity. However, the pretreatment either in air or in Ar has no any effects on the activity of propane conversion on 28V-Mg-O catalyst.

To investigate the catalytic properties of alkali metal loaded 28V-Mg-O, it can be observed that the catalytic performance of all alkali metal loaded 28V-Mg-O is different from that of unpromoted 28V-Mg-O. Pretreatment of catalyst loaded with a small amount of alkali metals in air or Ar affects the activity of catalyst , which is decreased at the high reaction temperature, due to alkali metals is inserted into the catalyst structure in the VO_3 position which involves the activity of the catalyst. Alkali metal in the catalyst structure may disturb the adsorption of propane on the catalyst surface. This makes the activity of alkali metal loaded 28V-Mg-O decreases. However, the increasing of alkali metal content apart from resulting in the increase of the basicity of catalyst also enhances the oxidation of propane.

In the case of Li loading, the activity and the propene selectivity of catalyst pretreated in Ar are better than that of the catalyst pretreated in air. This may be the more basicity of the catalyst pretreated in Ar , may support the adsorption of propane on the basic surface of catalyst and can act as an inhibitor for the adsorption of propene.

Considering of Na loading, the activity of the catalyst pretreated in Ar is lower than that of the catalyst pretreated in air , but the propene selectivity is higher. It is hypothesized that the pretreatment of the Na loaded catalyst under the oxidizing atmosphere will change the catalyst structure to a more stable oxidized form which prefers to the oxidation of propene.

For K loading, the more basicity of catalyst pretreated in non-oxidizing atmosphere is the cause of the increasing of the activity and the propene selectivity in the catalyst pretreated in Ar. Thus, the catalyst pretreated in the non-oxidizing atmosphere provides better catalytic properties than the catalyst pretreated in the oxidizing atmosphere.

To determine the repeatability of the reaction of 28V-Mg-O, it can be found that the experiment of 28 V-Mg-O can be repeated. After the catalyst which is pretreated in air is used in the ODH reaction, the catalyst structure can be reversed to the oxidized form. Nevertheless, in the case of the catalysts pretreated in Ar , the catalytic structure may loss oxygen species from the catalyst surface and form a more stable structure which is difficult to reverse to the original oxidized form. The results obtained from the continuous run with pretreatment in different atmosphere (section 5.2.4) have shown that after 28 V-Mg-O loss some oxygen during the first pretreatment in Ar, its surface structure has changed to some extent resulted in changes in catalytic property. Switching pretreatment atmosphere still cannot recover its original catalytic property. Na loaded catalyst shows some different behaviors. After the first pretreatment in Ar, the catalyst activity changes to a new value. Subsequent pretreatment did not result in any change in the catalytic property. This means that Na may increase transformation rate of the V-Mg-O layer to become a new stable structure within only the first pretreatment period. This result is agree with the paper of Kung and colleagues (1996a) who have concluded that the presence of residual alkali in the oxide catalyst can increase the thermal stability of stable compound.