CHAPTER V

RESULTS AND DISCUSSION

This chapter is divided in to five sections : section 5.1 reports composition and surface area of catalyst. Blank test for homogeneous reaction is shown in section 5.2. Section 5.3 describes the results of X-ray diffraction pattern (XRD) and Fourier Transform Infrared (FT-IR) analysis. Effect of catalyst loading, and catalytic behavior of the optimum catalyst are presented in section 5.4 and 5.5, respectively.

5.1 Composition and surface area of catalyst

The vanadium content of catalysts investigated measured by atomic adsorption spectroscopy (AAS) and BET surface area, are shown in Table 5.1 below.

Table 5.1 List of the vanadium content and BET surface area of catalyst

Type of catalyst	Vanadium content (wt.% V_2O_5)	Surface area (m^2/g)
TiO_2	0.0	10.6
5 V_2O_5/TiO_2	4.6	10.8
9 V_2O_5/TiO_2	8.8	11.3
13 V_2O_5/TiO_2	12.5	11.6
18 V_2O_5/TiO_2	17.7	12.8
23 V_2O_5/TiO_2	22.3	13.6
27 V_2O_5/TiO_2	26.4	12.5
V_2O_5	100.0	10.4

The above data show that when increases vanadium loading, surface area slightly increases but up to a maximum at about 23 wt.% V_2O_5. Many studies which used V_2O_5 supported over TiO_2 with a high surface area [11-14, 17, 22, 24-28] also found that surface area slightly increased with amount of vanadium on the surface and decreased at too high loadings [11-14]. At present there is no explanation for this phenomenon.

5.2 XRD and FT-IR analysis

Figure 5.1 shows X-ray diffraction patterns of TiO_2, V_2O_5, and V_2O_5/TiO_2 catalysts, respectively. XRD analysis of all sample show that at low V_2O_5 loading only TiO_2 (anatase) can be observed. The crystalline V_2O_5 appears as a shoulder for the 13 wt.% V_2O_5 and their intensity progressively increases with increasing the V_2O_5 loading. The XRD results suggest that at vanadium loading less than about 13 wt.% V_2O_5 does not appear as large crystalline V_2O_5.

Results of FT-IR spectrum is exhibited in Figure 5.2. The major IR bands of the anatase phase of TiO_2 appear at about 640 and 860 cm^{-1}, while the major IR bands of V_2O_5 exhibit around 492, 614, 833, and 1022 cm^{-1}. The IR band around 1022 cm^{-1} has been assigned to the V=O stretching vibration of bulk V_2O_5 [34]. When compare IR band for all catalyst loading, the prominent IR band around 1022 cm^{-1} appears when vanadium loading reaches 5 wt.% and their intensity gradually increases with the increase of V_2O_5 loading. In addition to IR band around 833 cm^{-1}, characteristic of V_2O_5 can be observed as a shoulder for the 9 V_2O_5/TiO_2 and the intensity gradually increases as increasing the V_2O_5 loading. The characteristic IR band of TiO_2 gradually disappears and can not be observed when V_2O_5 loading is increased up to 23 wt.% V_2O_5. The disappearance of TiO_2 IR bands shows that the surface of TiO_2 is completely covered by V_2O_5 surface species.

The results of XRD analysis combined with FT-IR experiment indicate that the formation of crystalline V_2O_5 starts well before the surface of TiO_2 is completely covered by V_2O_5 surface species.

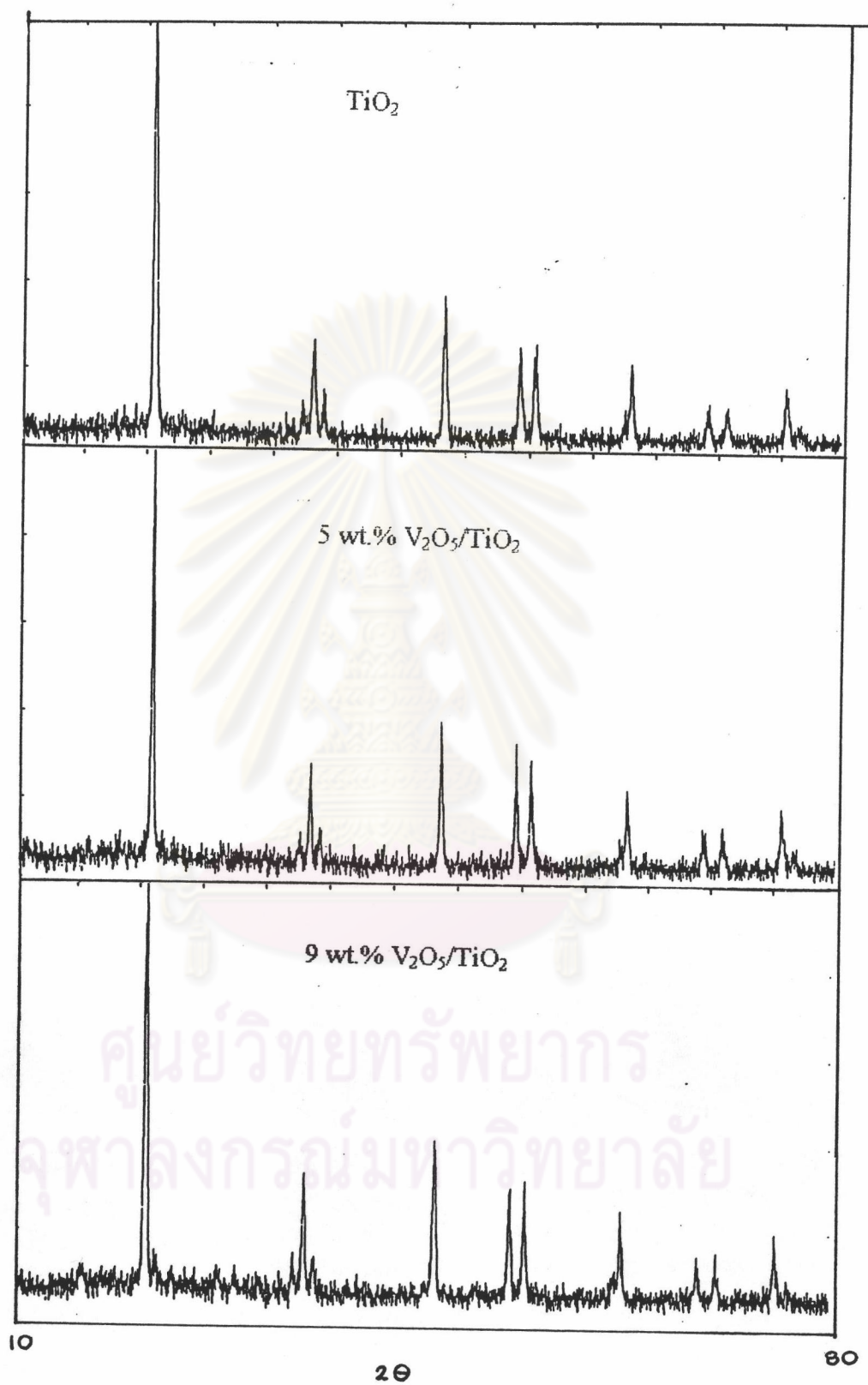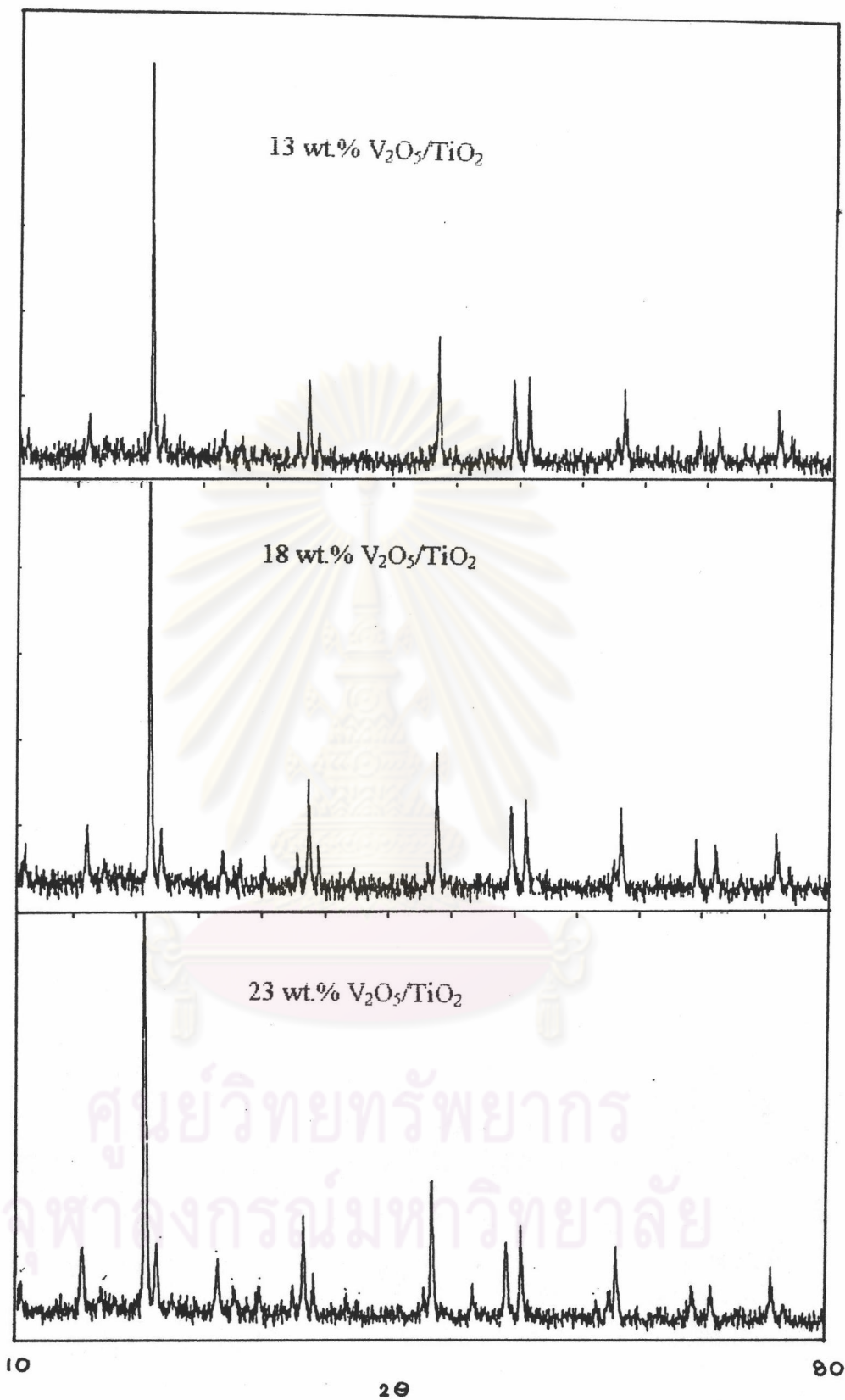**Figure 5.1(a)** X-ray diffraction (XRD) pattern of TiO_2 , 5, 9 wt.% V_2O_5/TiO_2

Figure 5.1(b) X-ray diffraction (XRD) pattern of 13, 18, 23 wt.% V_2O_5/TiO_2
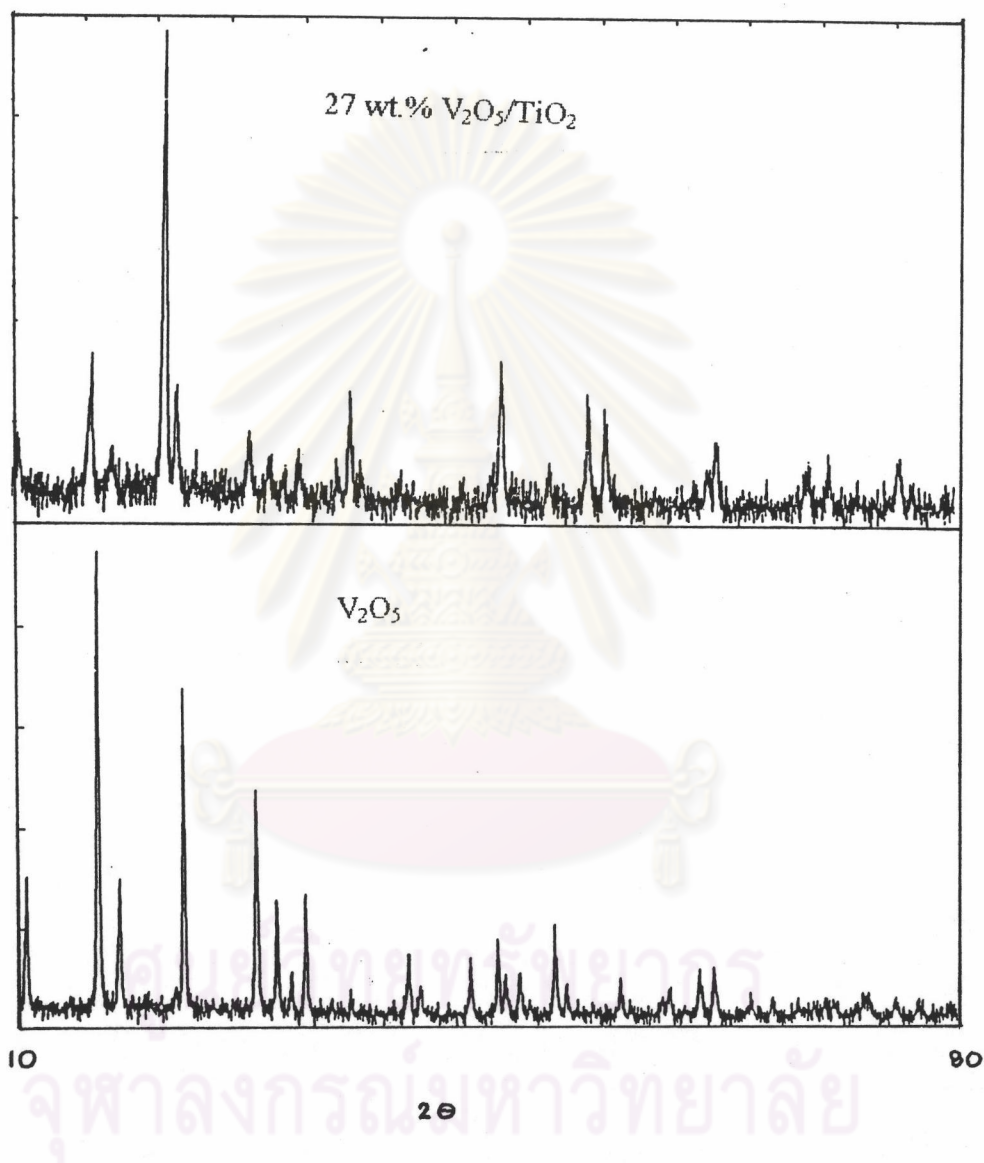
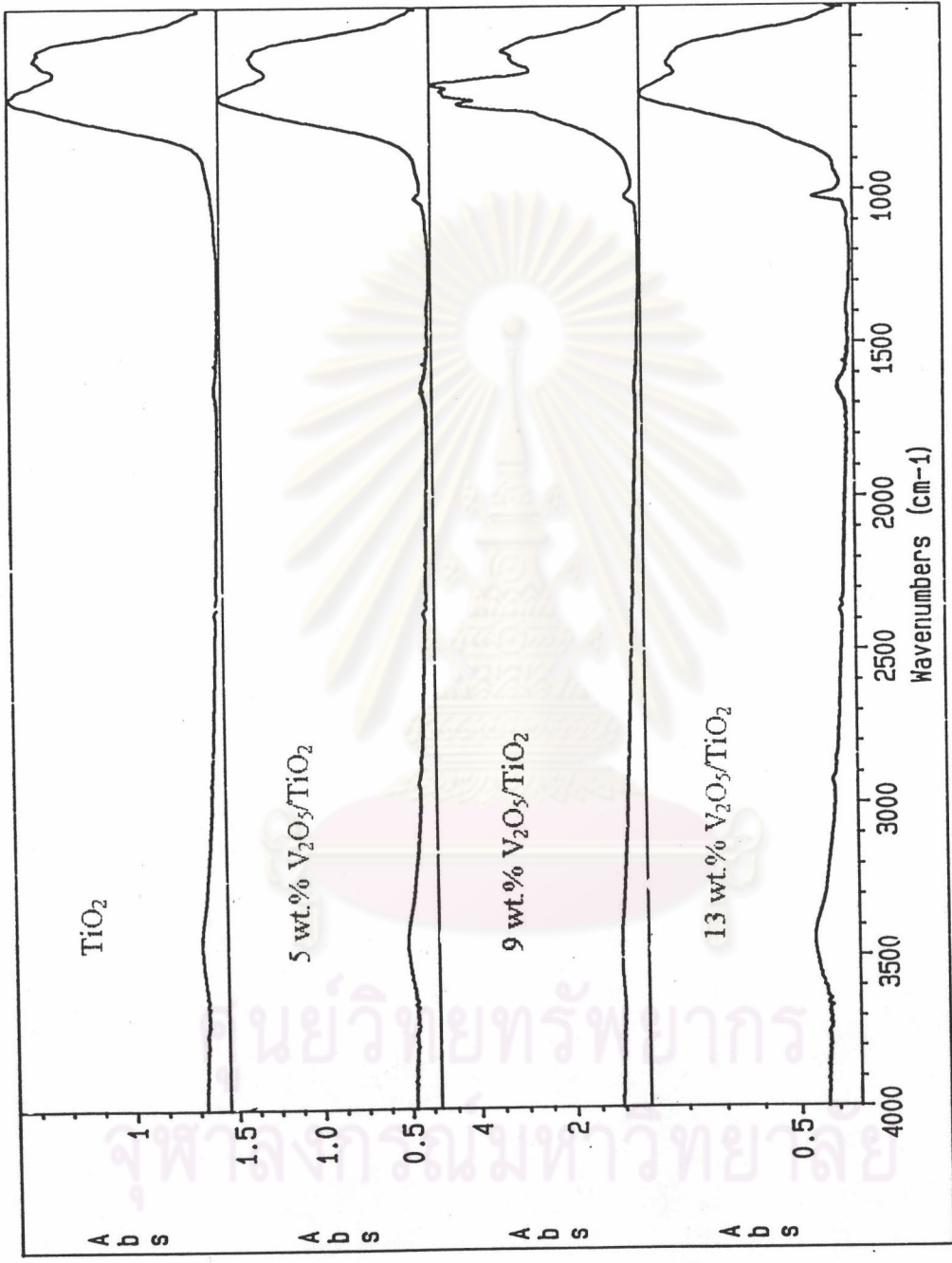**Figure 5.1(c)** X-ray diffraction (XRD) pattern of 27 wt.% V_2O_5/TiO_2 and V_2O_5

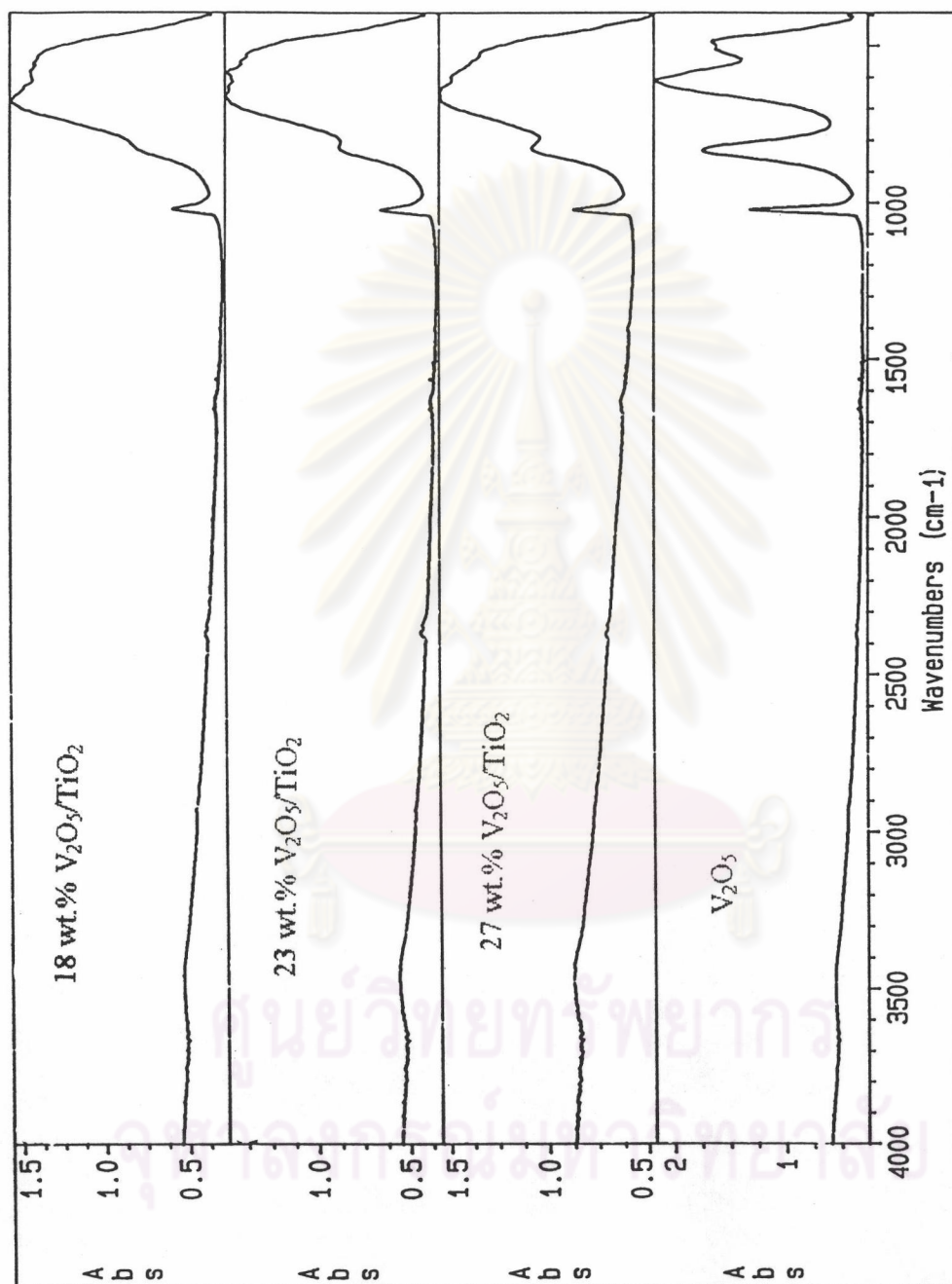**Figure 5.2(a)** FT-IR spectra of TiO_2, 5, 9, 13 wt.% V_2O_5/TiO_2

Figure 5.2(b) FT-IR spectra of 18, 23, 27 wt.% V_2O_5/TiO_2 and V_2O_5

5.3 Blank test for homogeneous reaction

The tube quartz and the quartz wool were tested for the catalytic activity of homogeneous reaction by performing blank reactor runs on several reactant gas (NO, $NO+O_2$, O_2+N_2, $NO+NH_3$, NH_3+O_2, and $NO+O_2+NH_3$) at temperatures in the range of 50 to 500 ^{o}C. The conversion of nitric oxide for homogeneous reaction is shown in Figure 5.3. This study shows that without NH_3 the NO conversion could not be observed in this temperature range. When NH_3 was added to the reactant gas, the experimental result shows that at reaction temperature lower than 350°C, homogeneous decomposition of NO is insignificant. Above 350°C the NO conversion begins to increase and reduces 12 % at 500°C. It should be noted here that NO conversion does not depend on the presence of O_2 in the reactant gas. This conclusion comes from the observation that when O_2 was added to the mixture of $NO+NH_3$, no change in NO conversion was observed. This result means that NO directly reacts with NH_3 without O_2 involving.
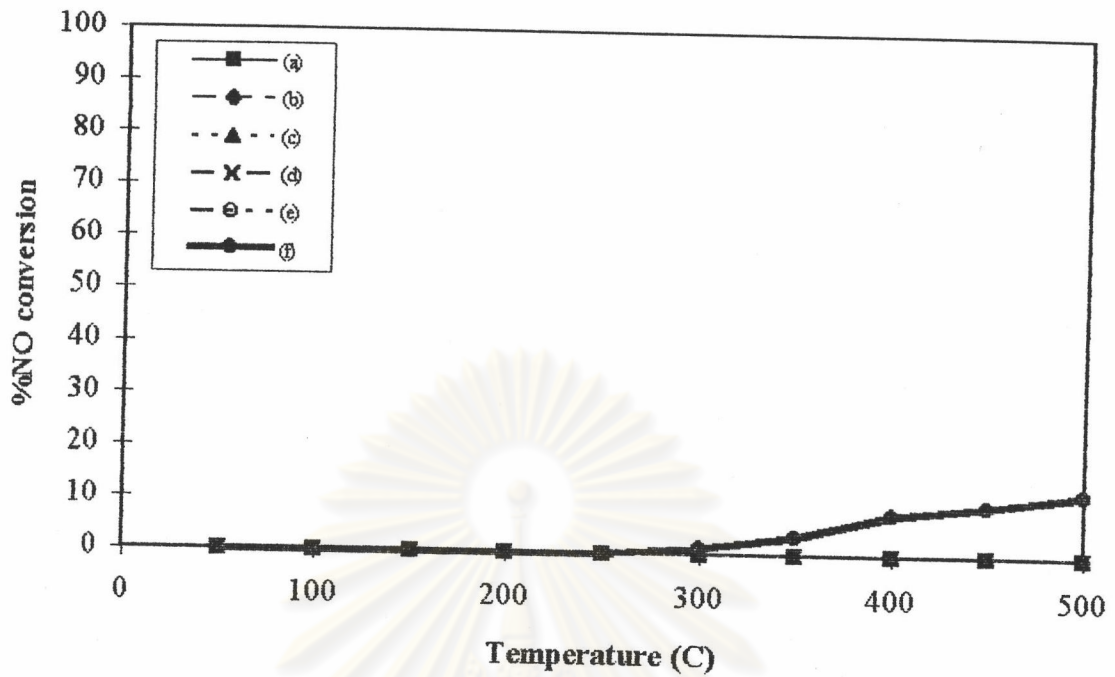
Figure 5.3 The conversion of nitric oxide for homogeneous reaction ; (a) NO,

(b) NO+O_2 , (c) O_2+N_2 , (d) NO+NH_3 , (e) NH_3+O_2 , and
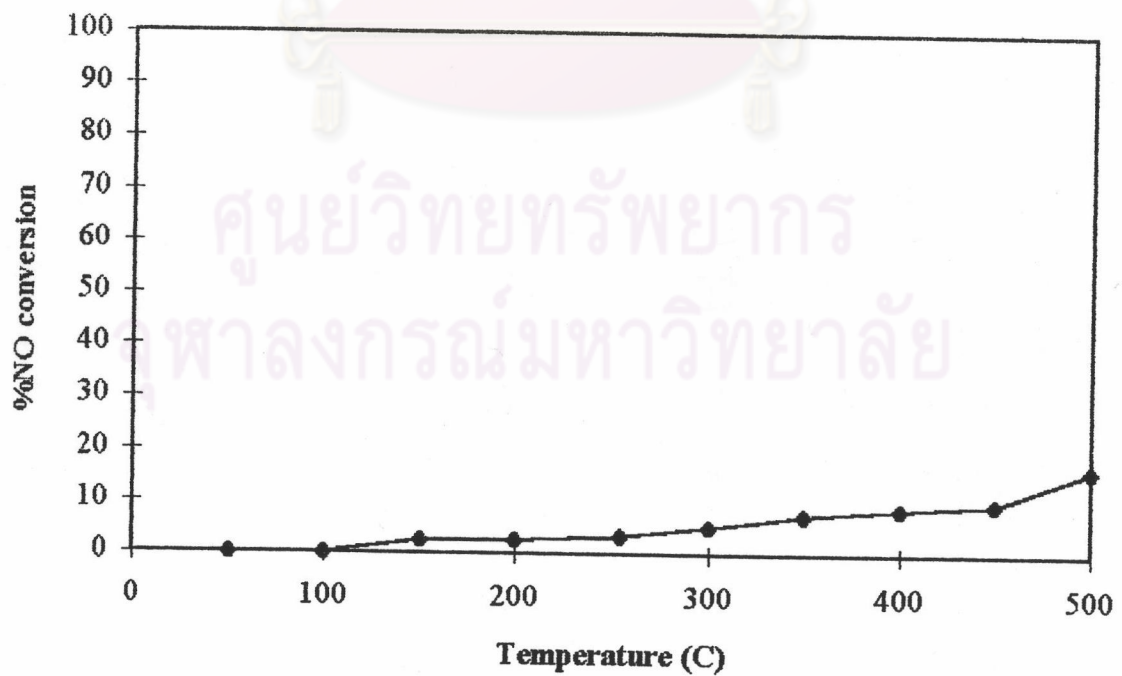
(f) NO+NH_3+O_2 conditions.

Figure 5.4 Result of SCR activity for TiO_2

5.4 Effect of catalyst loading

This section investigates the effect of V_2O_5 loading over vanadia-titania catalyst for the reduction of NO_x. The experiment was performed in the temperature range of 50 to 500^oC which the reactant gas feed concentration were kept constant at 500 ppm NO, 500 ppm NH_3, and 2 vol.% O_2, respectively. Figure 5.4 shows the relationship between SCR activity (expressed as %NO conversion) and the reaction temperature for TiO_2. The NO conversion gradually increases with increasing temperature from 100^oC. However, when compare to the homogeneous decomposition (see Figure 5.3), it can be concluded that TiO_2 support has very low activity for the SCR condition.

The SCR activity of V_2O_5 is shown in Figure 5.5. The NO conversion gradually increases with increasing temperature until the maximum NO conversion is reached at temperature about 400^oC and before slightly decreases. This decrease is caused by the direct oxidation of ammonia to nitric oxide which takes place over crystalline V_2O_5. When compare to TiO_2 support, it can be concluded that V_2O_5 has a slightly higher activity.

When 5 wt.% V_2O_5 was added to TiO_2 support, it was observed the NO conversion can be observed at reaction temperature as low as 50^oC, following by gradually increases until the maximum NO conversion is reached at temperature around 400^oC (as shown in Figure 5.6). Then the NO conversion decrease to zero at
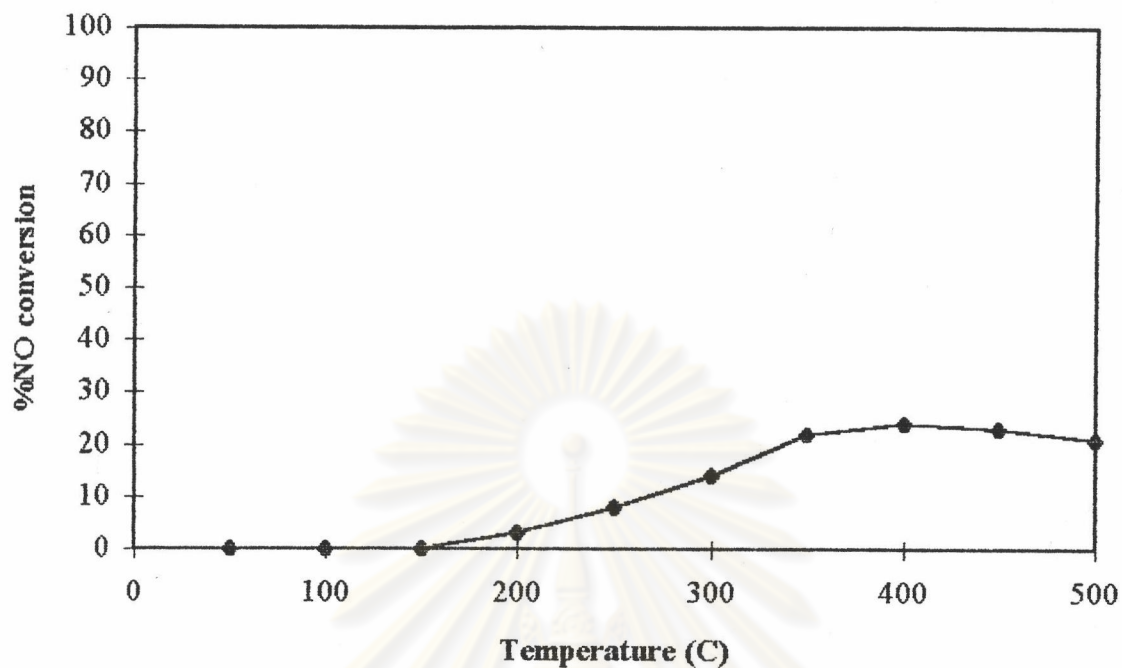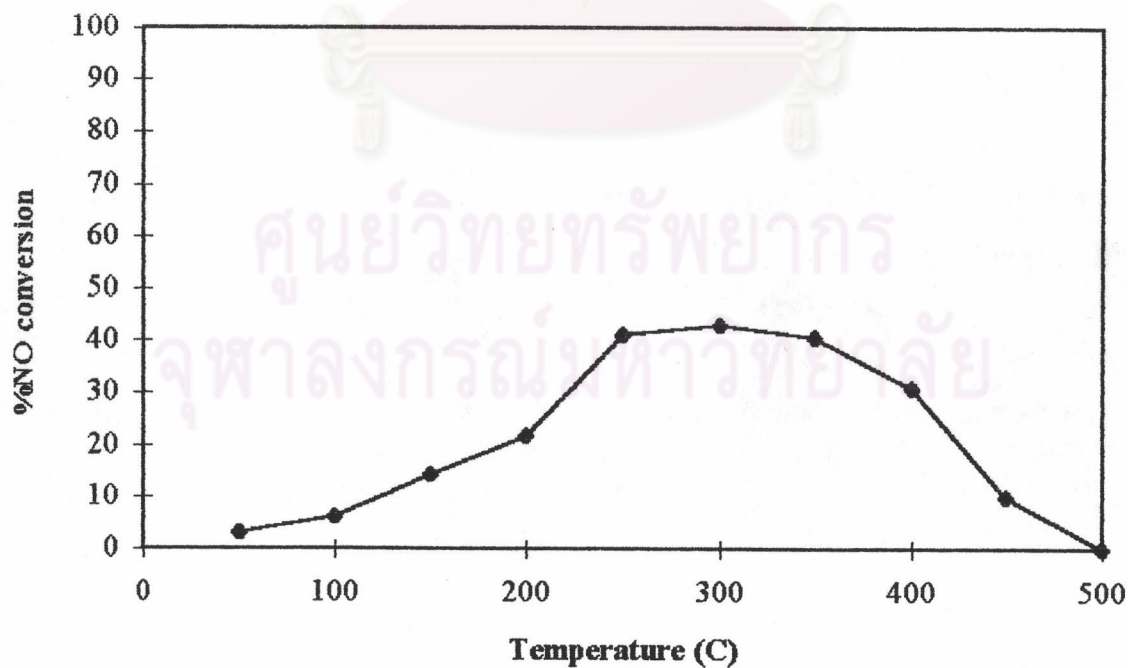
Figure 5.5 Result of SCR activity for V_2O_5

Figure 5.6 Result of SCR activity for 5 wt.% V_2O_5/TiO_2

temperature 500°C. When compare to TiO_2 support and V_2O_5, it was found that dispersed V_2O_5 species has higher activity than bulk V_2O_5 or TiO_2 support especially at lower temperature. This result suggests that dispersion of V_2O_5 on TiO_2 changes catalytic property of V_2O_5 dramatically.

The catalytic property of 9 wt.% V_2O_5/TiO_2 is shown in Figure 5.7. In this case, it was found that the relationship between NO conversion and reaction temperature is similarly to that of 5 wt.% V_2O_5/TiO_2 catalyst, but with 10-20 % higher in conversion. The SCR activity of 13 wt.% V_2O_5/TiO_2, which has similar behavior, is shown in Figure 5.8. It was found that NO conversion gradually increases with increasing reaction temperature until the maximum NO conversion is reached (about 60%) at temperature around 350°C before continuously decreases.

Addition of V_2O_5 loading up to 18 wt.% V_2O_5, can increases NO conversion up to 80% at 250°C before gradually decreases, as shown in Figure 5.9.

Figure 5.10 shows the SCR activity of 23 wt.% V_2O_5. It was found that NO conversion rapidly increases with increasing reaction temperature until the maximum NO conversion is reached at temperature 400°C and before slightly decreases at higher reaction temperature. When compare to 18 wt.% V_2O_5, it was observed that for the temperature range of 50-250°C the NO conversion is slightly lower but at the reaction temperatures over 250°C the NO conversion is clearly higher. This effect is caused by different structures of the catalysts, monolayer and crystalline V_2O_5.
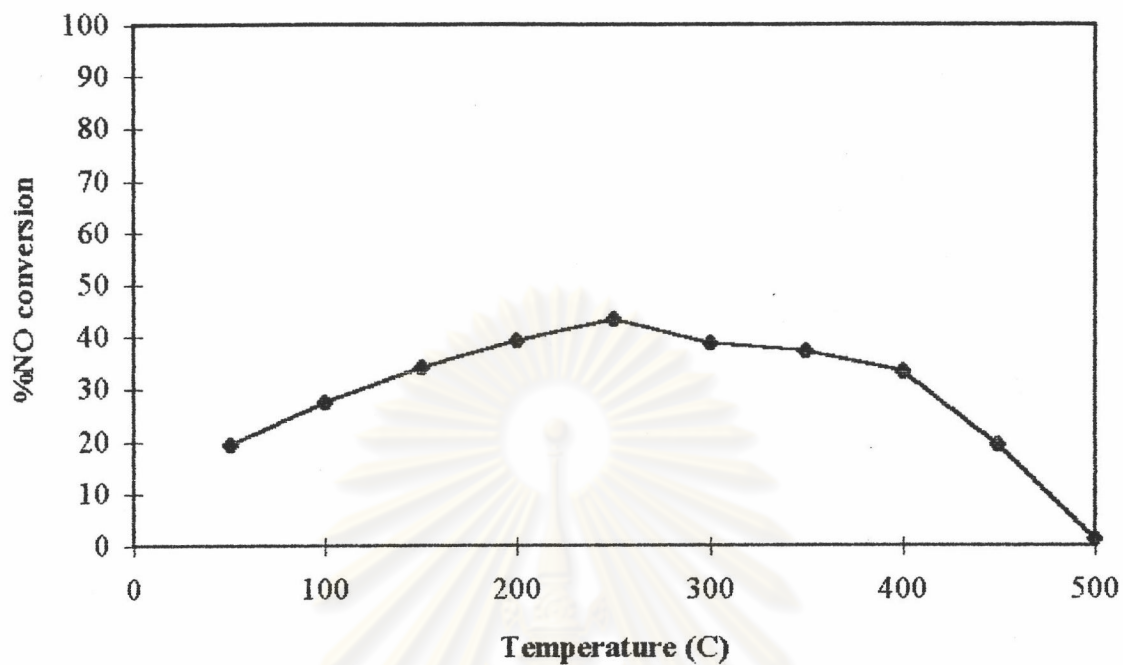
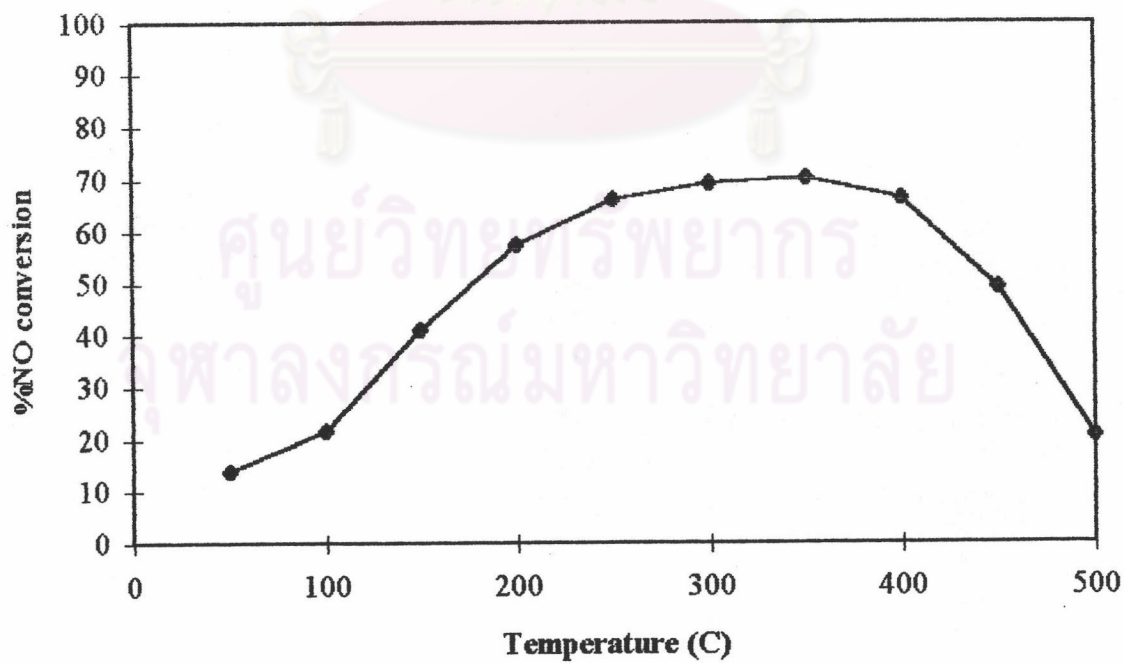**Figure** 5.7 Result of SCR activity for 9 wt.% V_2O_5/TiO_2

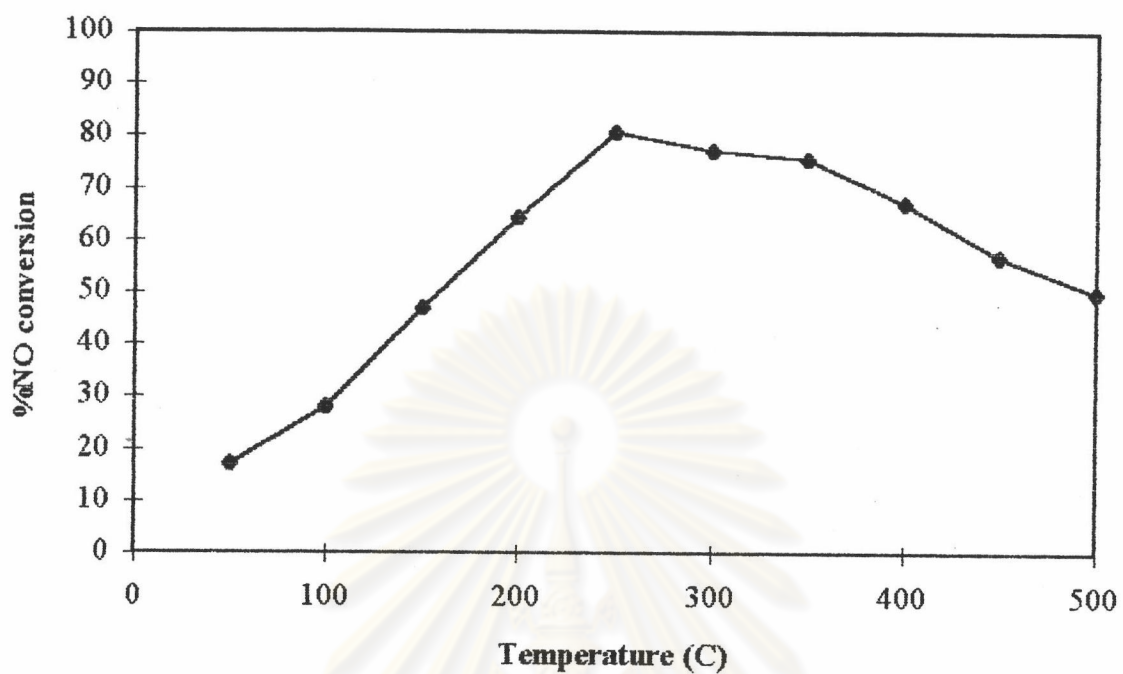**Figure 5.8** Result of SCR activity for 13 wt.% V_2O_5/TiO_2

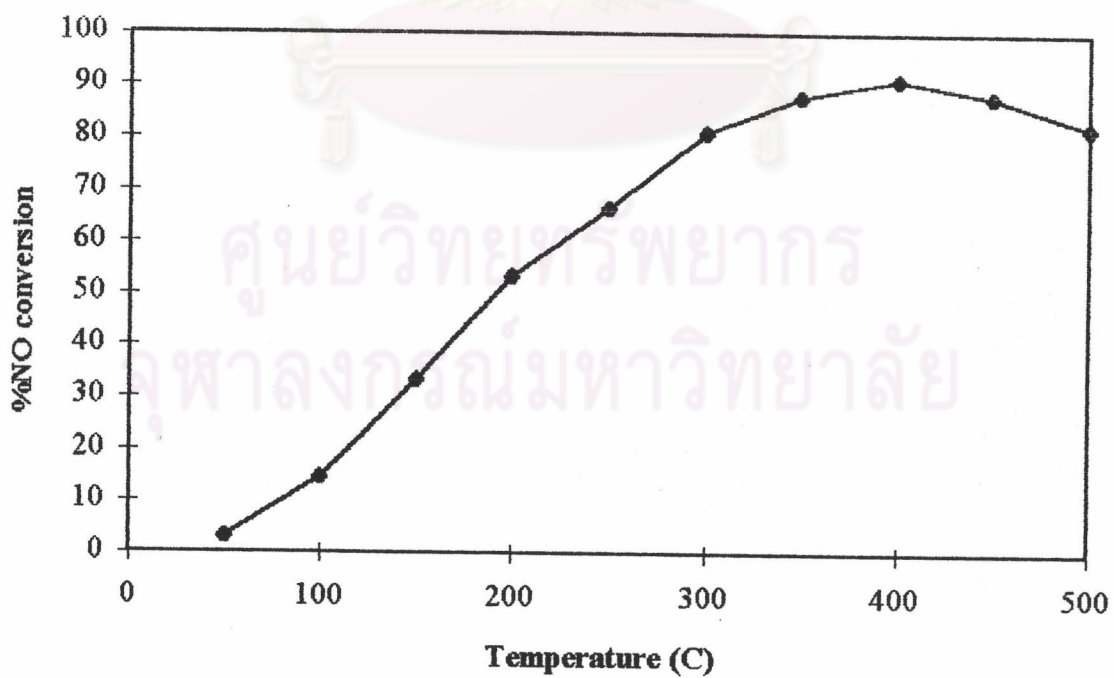**Figure 5.9** Result of SCR activity for 18 wt.% V_2O_5/TiO_2

Figure 5.10 Result of SCR activity for 23 wt.% V_2O_5/TiO_2

When V_2O_5 loading was increased up to 27 wt.% V_2O_5, it was found that NO conversion gradually increases with reaction temperature until reaching a maximum at reaction temperature about $400^{\circ}C$ (about 40%) and then slightly decreases in Figure 5.11. When compare to 23 wt.% V_2O_5, it can be observed the activity of 27 wt.% V_2O_5 is less active. The lower conversion is due to too high amount of crystalline V_2O_5.

Figure 5.12 shows the comparison between SCR activity versus V_2O_5 loading. The observed NO conversion at lower temperature $(50-250^{\circ}C)$ gradually increases with increasing the amount of V_2O_5 loading until a level of 13 wt.% V_2O_5 is reached and then continuously decreases even V_2O_5 loading increases. As for higher temperature $(300-500^{\circ}C)$, NO conversion progressively increases with increasing the amount of V_2O_5 loading until the maximum NO conversion is reached at about 23 wt.% V_2O_5 and further sharply decreases with further increase in V_2O_5 loading. This effect is probably caused by different structures of the catalyst. Due to the characteristic structure of catalyst with V_2O_5 loading over 23 wt.% V_2O_5 which has crystalline V_2O_5 present more than catalyst with lower V_2O_5 loading. The above data can be concluded that bulk V_2O_5 is less active than dispersed V_2O_5 species. For the SCR, therefore, the NO conversion of 13 wt.% V_2O_5 goes through a maximum in temperature range $50-250^{\circ}C$. Above $250^{\circ}C$, it was found that 23 wt.% V_2O_5 gives the maximum NO conversion. The phenomenon is caused by different structure of catalyst also, which influences the direct oxidation of ammonia to NO_x. This is because crystalline V_2O_5 is less active for the direct oxidation of ammonia when

compare to dispersed V_2O_5 species [16]. Therefore, it can be concluded that the NO conversion of 23 wt.% V_2O_5 goes through a maximum due to the presence of crystalline V_2O_5 do not seem to affect the direct oxidation of ammonia significantly in temperature range 300-500°C.

Finally, it can be concluded that 23 wt.% V_2O_5 is the optimum catalyst because of it can use in wider range of reaction temperature.
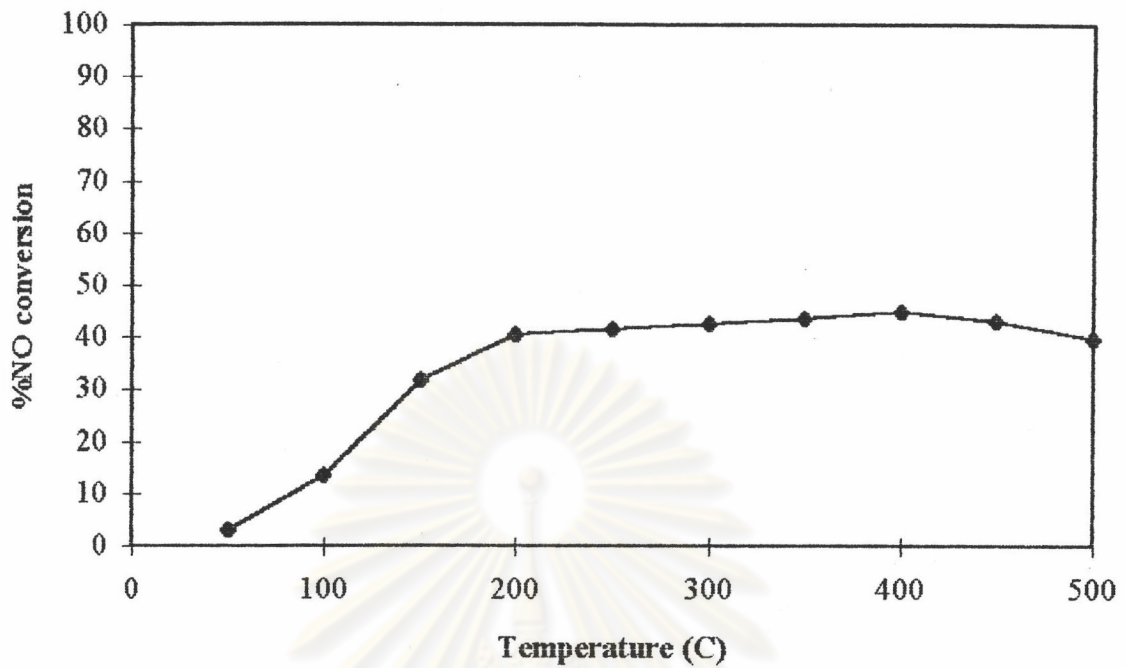
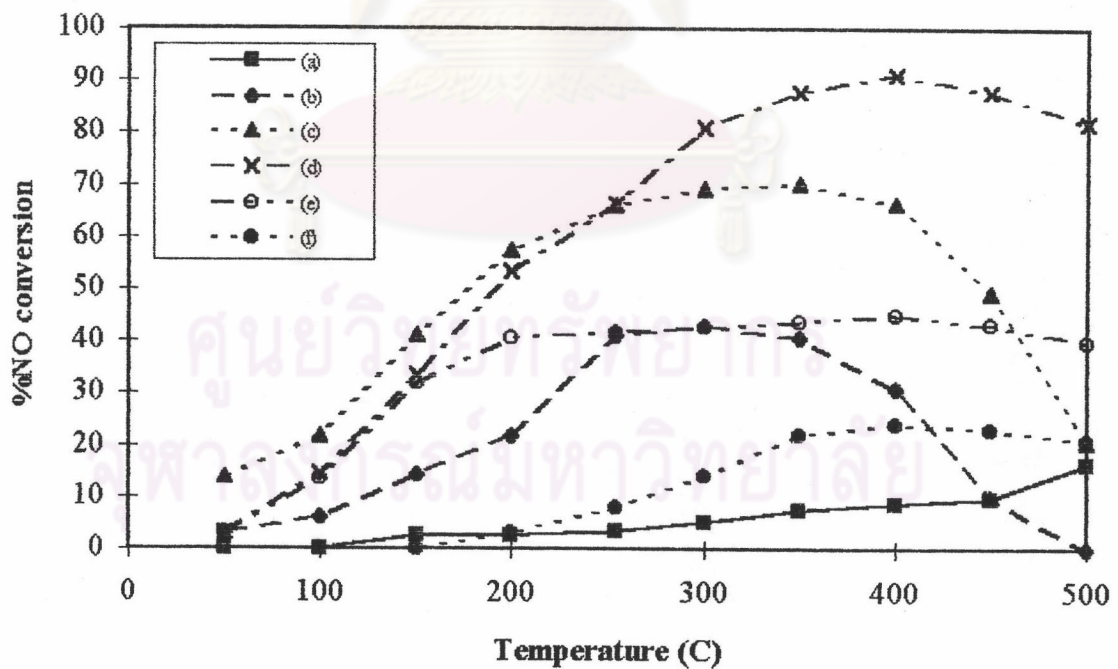**Figure 5.11** Result of SCR activity for 27 wt.% V_2O_5/TiO_2

Figure 5.12 Result of the comparison of SCR activity for catalyst loading ; (a) TiO_2 ,

(b) 5 wt.% V_2O_5/TiO_2, (c) 13 wt.% V_2O_5/TiO_2 , (d) 23 wt.% V_2O_5/TiO_2 ,

(e) 27 wt.% V_2O_5/TiO_2 , and (f) V_2O_5

5.5 The catalytic behavior of the optimum catalyst

From the results of previous section, it can be concluded that an optimum catalyst is 23 wt.% V_2O_5. The catalytic behavior of 23 wt.% V_2O_5 catalyst under operating condition for several reactant gas, NO, NO+O_2, NO+NH_3, NO+O_2+NH_3, and NH_3+O_2 was further investigated. Preliminary study under the presence of SO_2 and H_2O was also performed in the reaction temperature range of 50-500°C. Figure 5.13 shows the SCR activity versus reaction temperature under NO, NO+O_2 , NO+NH_3 , and NO+O_2+NH_3 conditions. Under the presence of only NO, the NO conversion gradually increases with increasing temperature especially at temperature above 300°C, which indicates that 23 wt.% V_2O_5 can directly decompose NO. When O_2 was added to the reactant gas, the NO conversion slightly decreases when compare to the presence of only NO.   This effect is caused by oxygen gas suppress the nitric oxide decomposition.

In the case of NO+NH_3 condition, the NO conversion progressively increases with increasing reaction temperature. When compare to the case of NO and NO+O_2, the NO+NH_3 mixture can attain a higher NO conversion. When O_2 was added, the NO conversion rapidly increases with increasing temperature until the maximum NO conversion is reached at temperature about 400°C.   Ramis et al. [35] postulated the following mechanism for the reaction of NO and ammonia over V_2O_5/TiO_2 catalysts in the presence of oxygen under dilute gas conditions to explain this phenomenon ;

step 1 : ammonia is first strongly adsorbed adjacent to V=O as NH_4^+(ad)

step 2 : gaseous NO reacts with NH_4^+(ad) according to an Eley-Rideal

   mechanism to form nitrogen, water, and V-OH

step 3 : V-OH species are eventually reoxidized to V=O by gaseous oxygen.

In condition of NH_3+O_2 reaction, NO was formed on 23 wt.% V_2O_5 at 400^oC and further progressively increases with increasing temperature. The result is shown in Figure 5.14. It means that $NO+NH_3+O_2$ condition for 23 wt.% V_2O_5 can lead to the formation of NO due to the direct oxidation of ammonia at temperature above 400 ^oC which leads to the decrease of NO conversion.

Figure 5.15 shows the comparison between the absence and presence of 50 ppm SO_2 in SCR condition. The present of SO_2 sharply decreases NO conversion (about 40-60%), but this effect does not seem to affect catalytic activity significantly in reaction temperature ranges of 50-100^oC.

Next, SO_2 deactivated catalyst was tested in SCR condition. . The results are presented in Figure 5.16. In this case, NO conversion reach a value between 30-40%, which is lower than that of catalyst before deactivated. This result means that some compounds may deposit on catalyst surface. After a treatment in high purity nitrogen at 400^oC for 2 hours, it was found that the relationship between NO conversion and reaction temperature is similarly to that of the catalyst after being deactivated by SO_2. However, after treatment at 500^oC for another 2 hours, the observed NO conversion
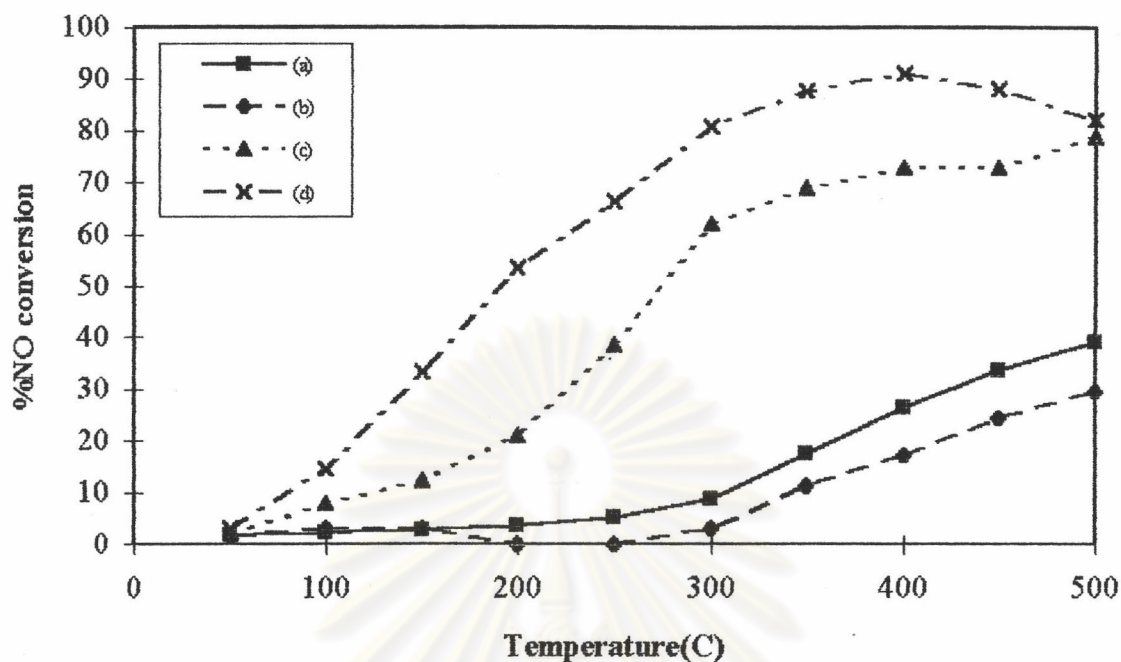
Figure 5.13 The SCR activity of 23 wt.% V_2O_5/TiO_2 under ; (a) NO, (b) $NO+O_2$,

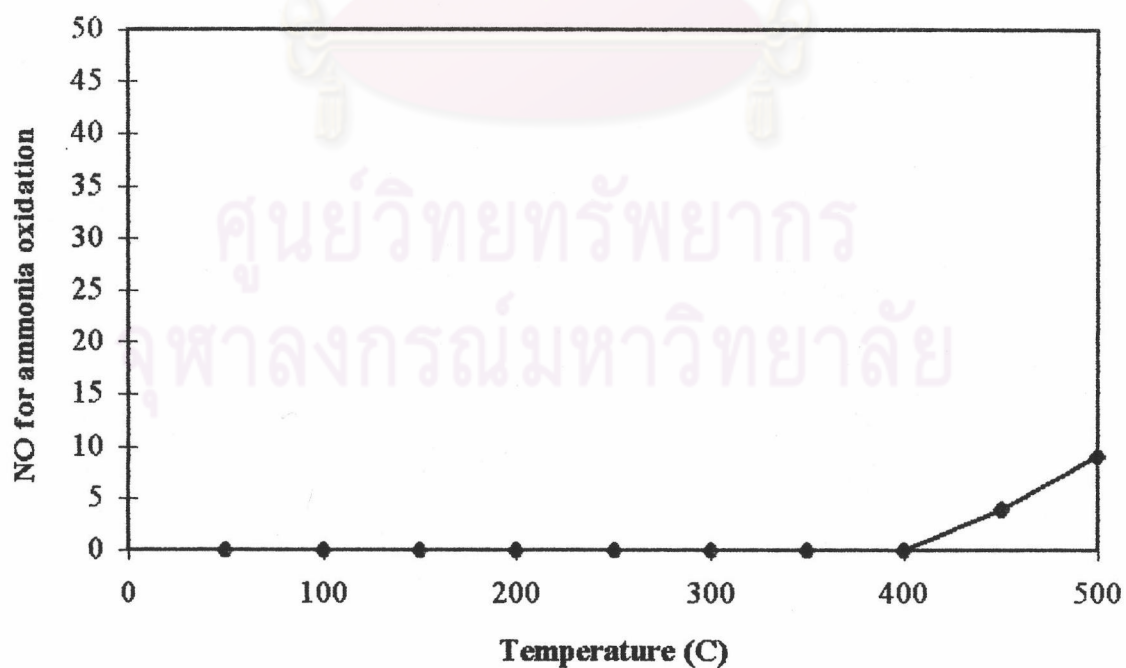(c) $NO+NH_3$, and (d) $NO+NH_3+O_2$ conditions

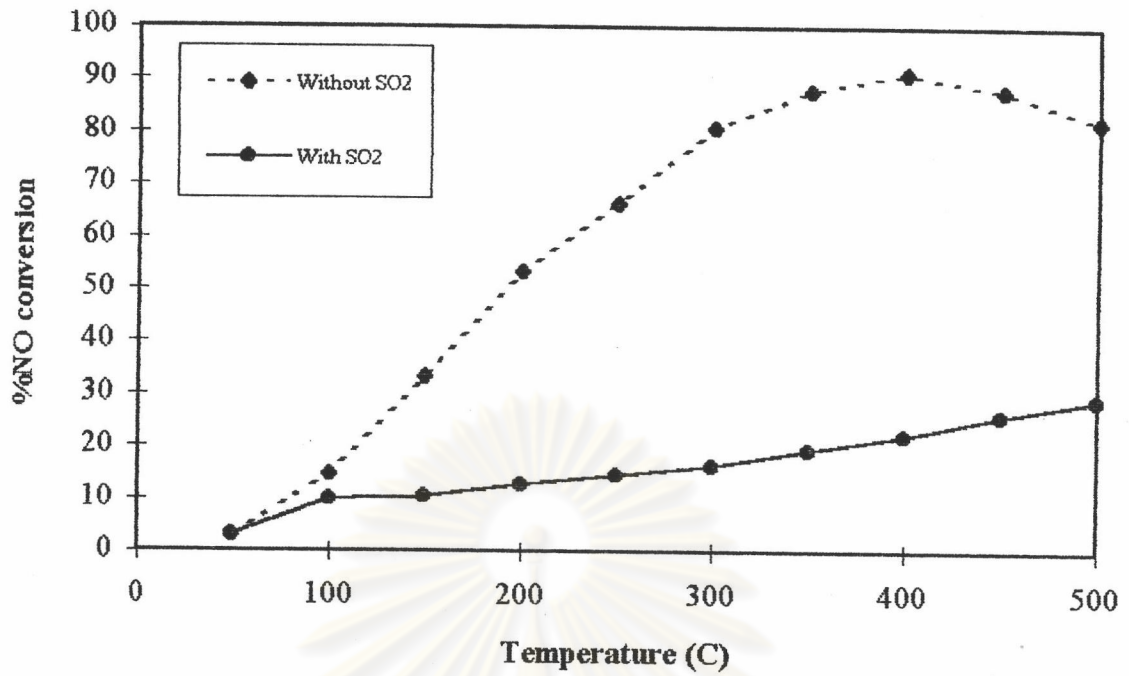**Figure 5.14** The NO for ammonia oxidation of 23 wt.% V_2O_5/TiO_2

Figure 5.15 Results of the comparison of SCR activity for 23 wt.% V_2O_5/TiO_2
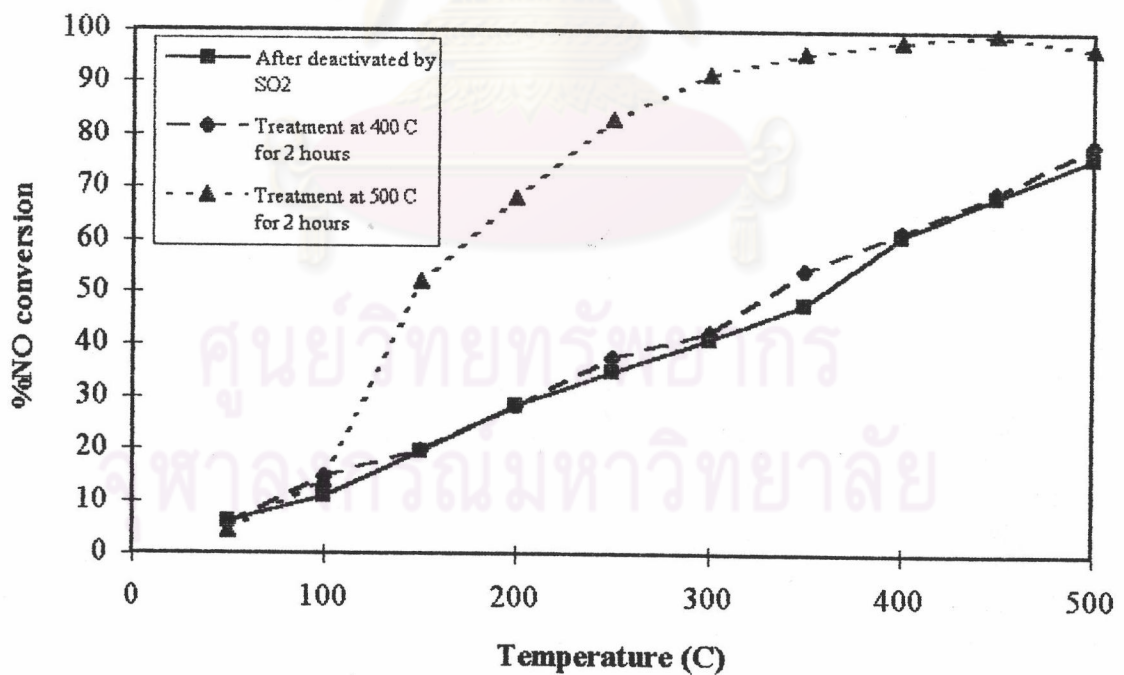
in the absence and presence of 50 ppm SO_2

Figure 5.16 Results of the comparison of SCR activity for 23 wt.% V_2O_5/TiO_2

after deactivated by SO_2 (a), after a treatment at 400°C for 2 hours (b),

and treatment at 500°C for 2 hours (c)

sharply increases with increase in reaction temperature and 10-20% higher in conversion at 500°C when compare to the result of the catalyst before deactivated and after treatment at 400°C for 2 hours. Since treatment at 500°C can increase NO conversion up to the value of the catalyst before being deactivated, therefore some strongly adsorb species may disappear from the catalyst surface. Thus it can be concluded that the catalyst after being deactivated by SO_2 should be regenerated by treatment at 500°C for 2 hours.

The presence of SO_2 can lead to reversible deactivation of catalyst, but no complete deactivation was observed. Kijlstra et al.[27] purposed that SO_2 oxidation which is the first reaction step leading to $(NH_4)_2SO_4$ deposition on catalyst, deactivates the catalyst. In order to confirm this hypothesis the deactivated catalyst and $(NH_4)_2SO_4$ were characterized by FT-IR. Results of FT-IR analysis are shown in Figure 5.17. The major IR bands of $(NH_4)_2SO_4$ appear around 3500-3100, 1408, 1100-1070, and 650 cm^{-1}. The IR bands around 3500-3100 and 1408 cm^{-1} have been assigned to NH_4^+ ion [36] while the IR bands around 1100-1070 and 650 cm^{-1} have been assigned to SO_4^{2-} group[36]. When comparing both IR spectra, there is no distinct characteristic IR bands of SO_4^{2-} group (around 1100-1070 and 650 cm^{-1}) in the spectrum obtained from the deactivated catalyst. Thus it was not likely that the hypothesis of $(NH_4)_2SO_4$ deposition is the major cause which leads to catalyst deactivation, but it can not be ruled out.
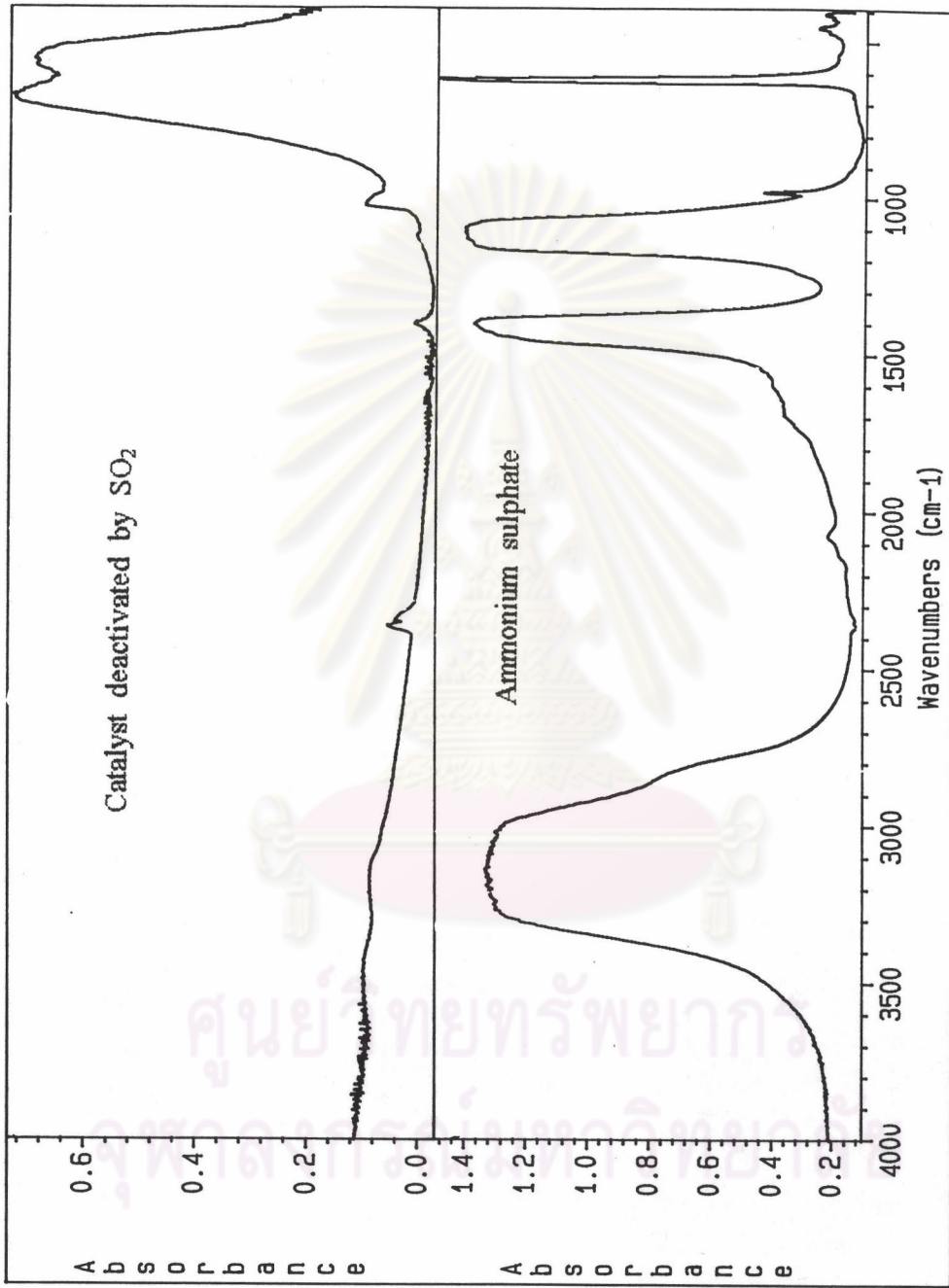
Figure 5.17 FT-IR spectra of 23 wt.% V_2O_5/TiO_2 after deactivated by SO_2 and ammonium sulphate

The other reason of catalyst deactivation may be the equilibrium SO_2 chemisorption on catalyst surface. But result of treatment at $400^{\circ}C$ for 2 hours does not agree with this hypothesis since there is no activity improvement. Another possible reason which can explain the deactivation of the catalyst may be the presence of different active site of the catalyst. Ozkan and Cai [16] have shown that crystal V_2O_5 has different crystal planes which have difference activity for the nitric oxide reduction. They investigated the kinetic of SCR reaction by performing experiment over V_2O_5 samples which preferentially exposed different crystal planes. The results showed major differences in activity and product distribution, suggesting that different crystal planes of vanadium pentoxide had different catalytic functions. Although they proposed that the ammonia adsorption was limited to V=O sites, which are located on the basal plane favor the direct oxidation of ammonia. On the other sites located on the side planes of V_2O_5, ammonia adsorption leading to SCR reaction can also take place. We may postulate there result that different plane of V_2O_5 may have difference resistance to SO_2 deactivation. SO_2 adsorption may take place on two types of site ; one being irreversible poisoned at low temperature, the other being reversible poisoned. Thus the SCR activity of the catalyst after deactivated to SO_2 is higher due to the disappear of reversible poison. However, the result of treatment at $500^{\circ}C$ for 2 hours indicated that the low temperature irreversible deactivation can be regenerated at $500^{\circ}C$ for 2 hours.

Figure 5.18 shows the SCR activity of 23 wt.% V_2O_5 under SCR condition without and with 10 vol.% H_2O. In the reaction temperature ranges of $50-100^{\circ}C$,

adding water seems not to affect catalytic activity significantly. For the reaction temperature above $100^{o}C$ the NO conversion in the presence of 10 vol.% H_2O is slightly lower than without H_2O. This may be caused by a competitive adsorption of water on active sites for ammonia adsorption thus decreasing the rate of reaction.

In the case of addition 10 vol.% H_2O and 50 ppm SO_2 , it was observed that the relationship between NO conversion and reaction temperature is similar to that of the case without water. The comparison is shown in Figure 5.19.
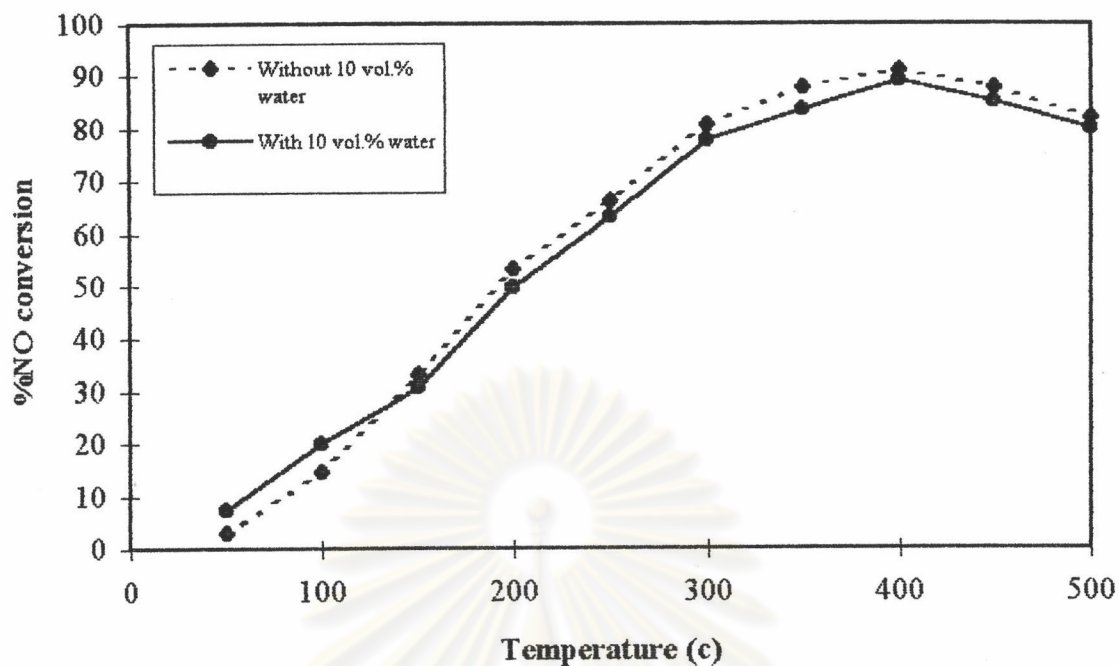
Figure 5.18 Results of the comparison of SCR activity for 23 wt.% V_2O_5/TiO_2
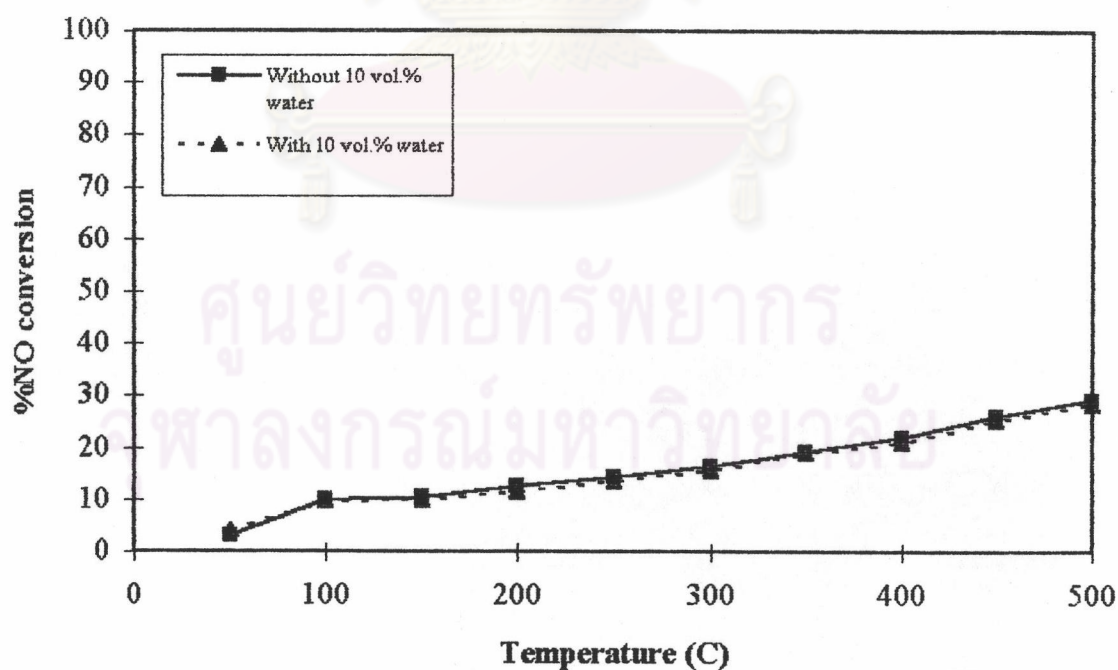
under SCR condition without and with 10 vol.% H_2O

Figure 5.19 Results of the comparison of SCR activity for 23 wt.% V_2O_5/TiO_2

in the absence and presence of 10 vol.% H_2O when SO_2 present