

## CHAPTER V

### RESULTS AND DISCUSSION

In this chapter, the results and discussion are divided into two major parts including the catalyst characterization and the catalytic test by the combustion of phthalic anhydride, maleic anhydride, acetic acid, benzene, toluene and ethyl benzene.

#### 5.1 Catalyst Characterization

##### 5.1.1 Determination of composition content of catalyst and surface area

The composition and the BET surface areas of all catalysts which are determined by AAS and BET surface area measurement are listed in Tables 5.1 and 5.2.

**Table 5.1** The composition of different magnesium loading catalyst and BET surface areas

Catalyst	%V <sup>a</sup>	%Mg <sup>b</sup>	Surface area (m <sup>2</sup> /g)
10V2MgOTi	9.46	4.4	12.34
10V4MgOTi	9.10	5.2	6.67
10V8MgOTi	9.25	7.3	5.10
MgTi	-	-	40.52
TiO <sub>2</sub>	-	-	55.18

\*The number in the catalyst symbol denotes the approximate weight percentage of V calculated as V<sub>2</sub>O<sub>5</sub>

<sup>a</sup>The content of vanadium is calculated in terms of % by weight of V<sub>2</sub>O<sub>5</sub>

<sup>b</sup>The content of magnesium is calculated in term of % by weight

**Table 5.2** The composition of different vanadium loading catalyst and BET surface areas

Catalyst	%*V <sup>a</sup>	%Mg <sup>b</sup>	Surface area (m <sup>2</sup> /g)
6V4MgOTi	5.3	3.2	6.23
8V4MgOTi	8.033	3.3	5.37
10V4MgOTi	9.10	5.2	6.67
12V4MgOTi	13.03	3.7	5.95
14V4MgOTi	13.75	5.1	7.25
16V4MgOTi	14.35	3.7	11.59
VTi	-	-	45.21

\*The number in the catalyst symbol denotes the approximate weight percentage of V calculated as V<sub>2</sub>O<sub>5</sub>

<sup>a</sup>The content of vanadium is calculated in terms of % by weight of V<sub>2</sub>O<sub>5</sub>

<sup>b</sup>The content of magnesium is calculated in term of % by weight

The data in Tables 5.1 and 5.2 show that the surface areas of VMgOTi catalysts are quite similar and relatively low. However, their surface areas slightly increase with increasing the content of vanadium. The similar behavior was reported by Teratrakoonwichaya (1996). The sequence of magnesium loading and the content of magnesium seem to have effect on the surface areas of the catalysts. When the content of magnesium was increased, their surface areas slightly decrease.

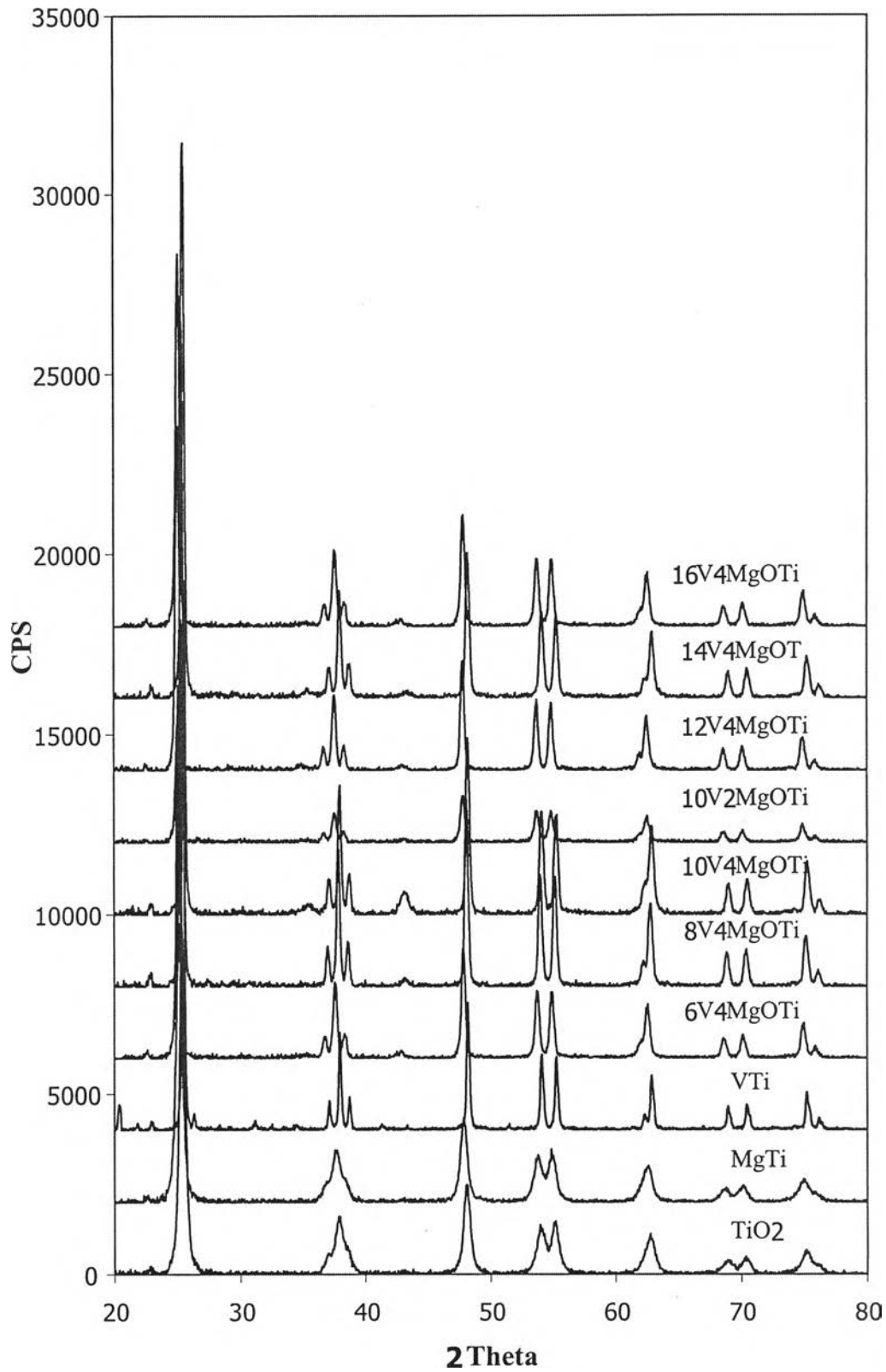
### 5.1.2 X-ray Diffraction

The crystal structure of all the catalysts was characterized by XRD. Figure 5.1 illustrates XRD spectra of  $\text{TiO}_2$ , VTi, MgTi and the various VMgOTi catalysts. XRD spectrum of  $\text{V}_2\text{O}_5$  shows three evident peaks at  $2\theta$  of  $20.5^\circ$ ,  $26.5^\circ$  and  $31^\circ$ . Comparison with VTi catalyst exhibited in this figure, the XRD spectrum of VTi shows peaks at the same position as  $\text{TiO}_2$  spectrum. However, the small peaks of crystalline  $\text{V}_2\text{O}_5$  at the  $2\theta$  values of  $20.5^\circ$  and  $26.5^\circ$  are observed.

From Figure 5.1, the spectrum of 10V2MgTi shows peaks at the same  $2\theta$  values as  $\text{TiO}_2$ . It can be seen that crystalline  $\text{V}_2\text{O}_5$  peaks can not be detected. That means the amount of vanadium oxides on 10V2MgTi surface may be not high enough to be determined by XRD or the vanadium oxide did not form a  $\text{V}_2\text{O}_5$  crystal structure on the  $\text{TiO}_2$  support.

The disappear of  $\text{V}_2\text{O}_5$  peak even the amount of V was as high as 16% suggested that V show form a new V-Mg-O component rather than  $\text{V}_2\text{O}_5$ . This conclusion comes from some reports showing that  $\text{V}_2\text{O}_5/\text{TiO}_2$  can show  $\text{V}_2\text{O}_5$  peaks when the amount of  $\text{V}_2\text{O}_5$  is only 18% [Teratrakoonwichaya].

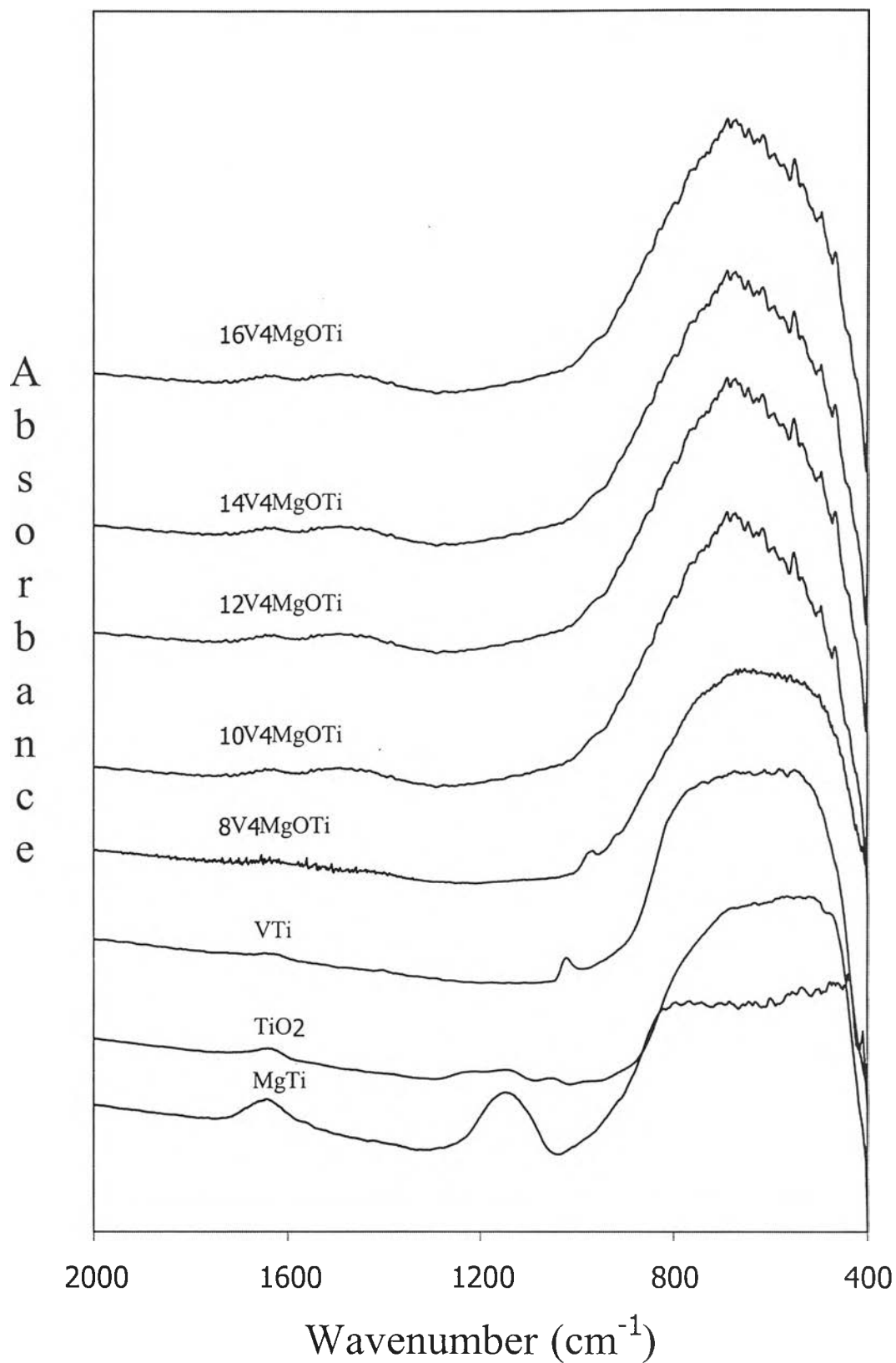
From the preparation method of 10V2MgTi,  $\text{V}_2\text{O}_5$  may first deposite on  $\text{TiO}_2$  surface after calcination at  $550^\circ\text{C}$ . Although the melting point of pure  $\text{V}_2\text{O}_5$  is  $700^\circ\text{C}$  when vanadia is dispersed on  $\text{TiO}_2$  surface, it can be melted at lower temperature and react with MgO to form a new oxide compound, V-Mg-O, not form vanadium oxide. For this reason, the crystalline  $\text{V}_2\text{O}_5$  peaks at  $20.5^\circ$ ,  $26.5^\circ$  and  $31^\circ$  disappear.



**Figure 5.1** X-ray diffraction of  $\text{TiO}_2$ ,  $\text{MgTi}$ ,  $\text{VTi}$  and the variation of  $\text{VMgOTi}$

### 5.1.3 Fourier Transform Infrared Spectrometer (FT-IR)

The functional group on the surface of VMgOTi catalyst can be identified by using infrared radiation in the wavelength of  $400\text{-}2000\text{ cm}^{-1}$ , which is the proper wavelength for determining the solid surface. Figure 5.2 presents IR spectra of  $\text{TiO}_2$  and VMgOTi catalysts. Strong absorption bands at  $580$  and  $680\text{ cm}^{-1}$  are observed. As presented in this figure, the IR spectra of all VMgOTi catalysts exhibits the absorption bands at the same position as  $\text{TiO}_2$ . This indicates that the amounts of vanadium and magnesium on  $\text{TiO}_2$  surface are much less to observe the changes in IR bands.



**Figure 5.2** IR spectra of MgTi, TiO<sub>2</sub>, VTi, the differentiations of VMgOTi catalysts

## 5.2 Catalytic reaction

### 5.2.1 Combustion of Phthalic anhydride

Phthalic anhydride comprises of an anhydride functional group and a benzene ring. It is a product in the oxidation of *o*-xylene. Phthalic anhydride is a raw material in chemical industries such as productions of polymer and plasticizers. Phthalic anhydride has a melting point around 129-131°C. Its molecular weight is 148.12. The combustion reaction is as follows:

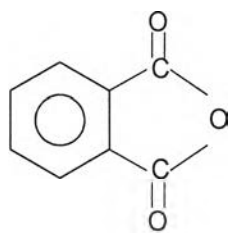
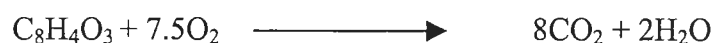


Figure 5.3 The structure of phthalic anhydride

In this research, the role of magnesium in the VMgOTi catalyst and the effect of different vanadium oxide and magnesium contents in the VMgOTi catalyst are investigated. Since the VMgOTi system is a novel system that have no information about its catalytic property, the oxidation properties of VMgOTi catalysts are studied by using the combustion reaction on phthalic anhydride and maleic anhydride as test reactions and the main products observed are only CO<sub>2</sub> and H<sub>2</sub>O.

*- Effect of magnesium loading*

Figure 5.4 shows the catalytic activity of 10V2MgOTi, 10VTi, 2MgTi, TiO<sub>2</sub> catalysts for phthalic anhydride combustion. For 10V2MgOTi catalyst, the conversion of phthalic anhydride increased from 5 to 81% at the temperature range of 200 to 400°C and steadily increased until the temperature reached 550°C, which the conversion was about 89%. On the other hand, TiO<sub>2</sub>, phthalic anhydride conversion enhanced from 4 to 82% and 10VTi, phthalic anhydride conversion enhanced from 4 to 78%. The conversion steadily increased from 3 to 64% at the temperature range of 200 to 550°C for 2MgTi catalyst.

2MgTi catalyst shows the phthalic anhydride conversion lower than TiO<sub>2</sub> support, indicating that magnesium was not able to catalyze the reaction. Moreover, it inhibited the ability to catalyze the reaction of TiO<sub>2</sub>. In the case of loading vanadium on TiO<sub>2</sub> such as 10VTi, it is shown that the conversion of phthalic anhydride did not improve comparing with unloaded TiO<sub>2</sub>. When loading both vanadium and magnesium into on TiO<sub>2</sub>, the phthalic anhydride conversion increased. The conversion was increased about 70% at the temperature range of 200 to 350°C for 10V2MgOTi, indicating that magnesium is able to improved the catalytic activity of 10V2MgOTi catalyst. The result reveals that loading magnesium into 10VTi catalyst to form a 10V2MgOTi catalyst gives a conversion increase about 25%.



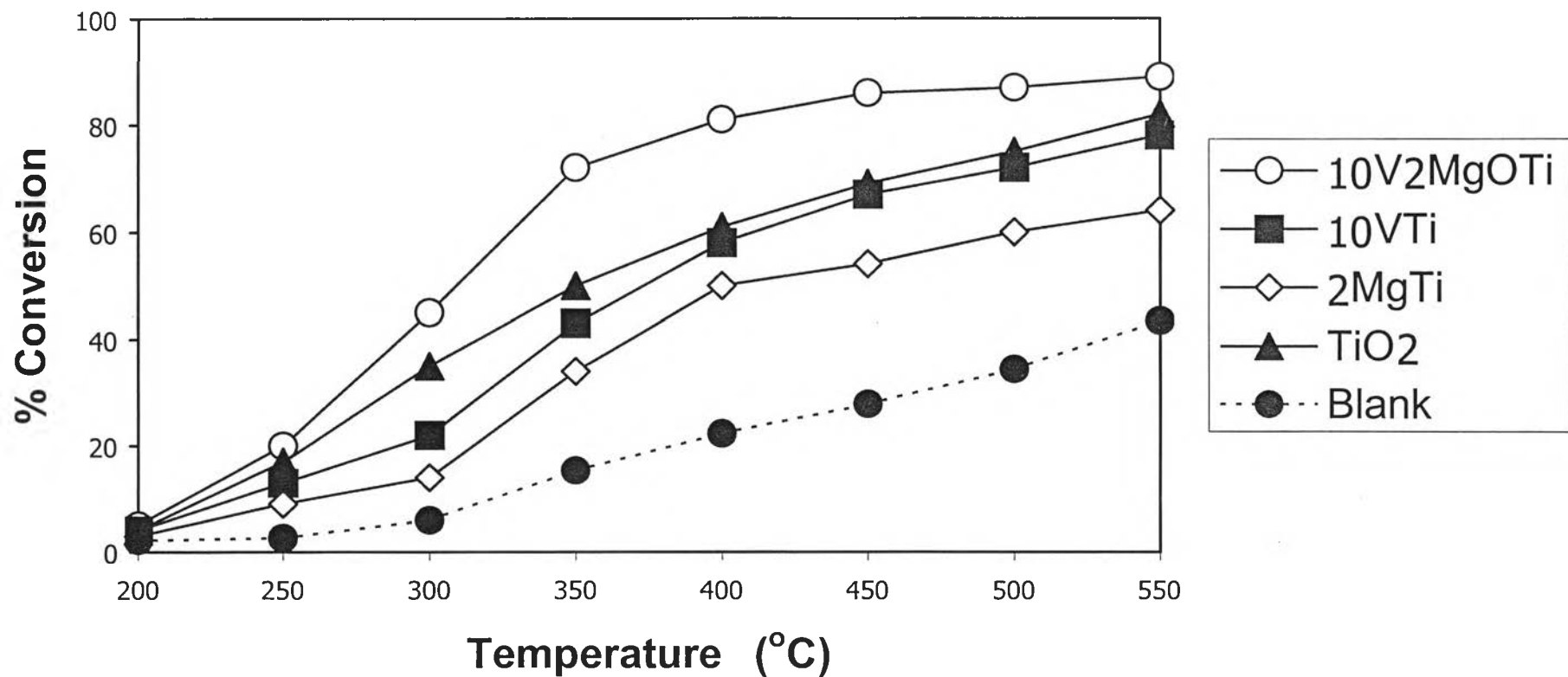


Figure 5.4 The result of phthalic anhydride combustions of 10V2MgTi, 10VTi, 2MgTi, TiO<sub>2</sub> and blank.

- *The optimum ratio of V:Mg on catalyst*

- *fixed V wt% with various Mg wt%*

Figure 5.5 shows the phthalic anhydride conversions over VMgOTi catalysts. The amount of V is fixed at around 10 wt%, while the amount of magnesium is varied to find the optimum amount of magnesium. It is found that 10V4MgOTi shows the best conversion, which increased from 6 to 80% in the range of temperature at 200 to 350°C and steadily raised until the temperature reached 550°C, which the conversion was about 90%. While 10V2MgOTi and 10V8MgOTi exhibit the phthalic anhydride conversion as about 3 to 88% and 3 to 82%, respectively, in the range of temperature 200 to 550°C. The catalytic activity of these catalysts is in the order of 10V4MgOTi > 10V2MgOTi > 10V8MgOTi.

- *fixed Mg wt% with various V wt%*

Figure 5.6 shows the phthalic anhydride conversion on the VMgOTi catalysts that fixed the amount of magnesium is fixed at 4 wt%, while the amount of vanadium oxide is varied to find the optimum amount of vanadium oxide. It was found that 10V4MgOTi shows the best conversion, which increases from 6 to 80% in the temperature range of 200 to 350°C. After that it slightly increases to 90% at 550°C. On the other hand, 6V4MgOTi, 8V4MgOTi, 12V4MgOTi, 14V4MgOTi and 16V4MgTi exhibit the conversion close to each other, about 4 to 85%. The catalytic activity of these catalyst is in the order of 10V4MgOTi > 14V4MgOTi > 12V4MgOTi > 8V4MgOTi > 6V4MgOTi > 16V4MgOTi.

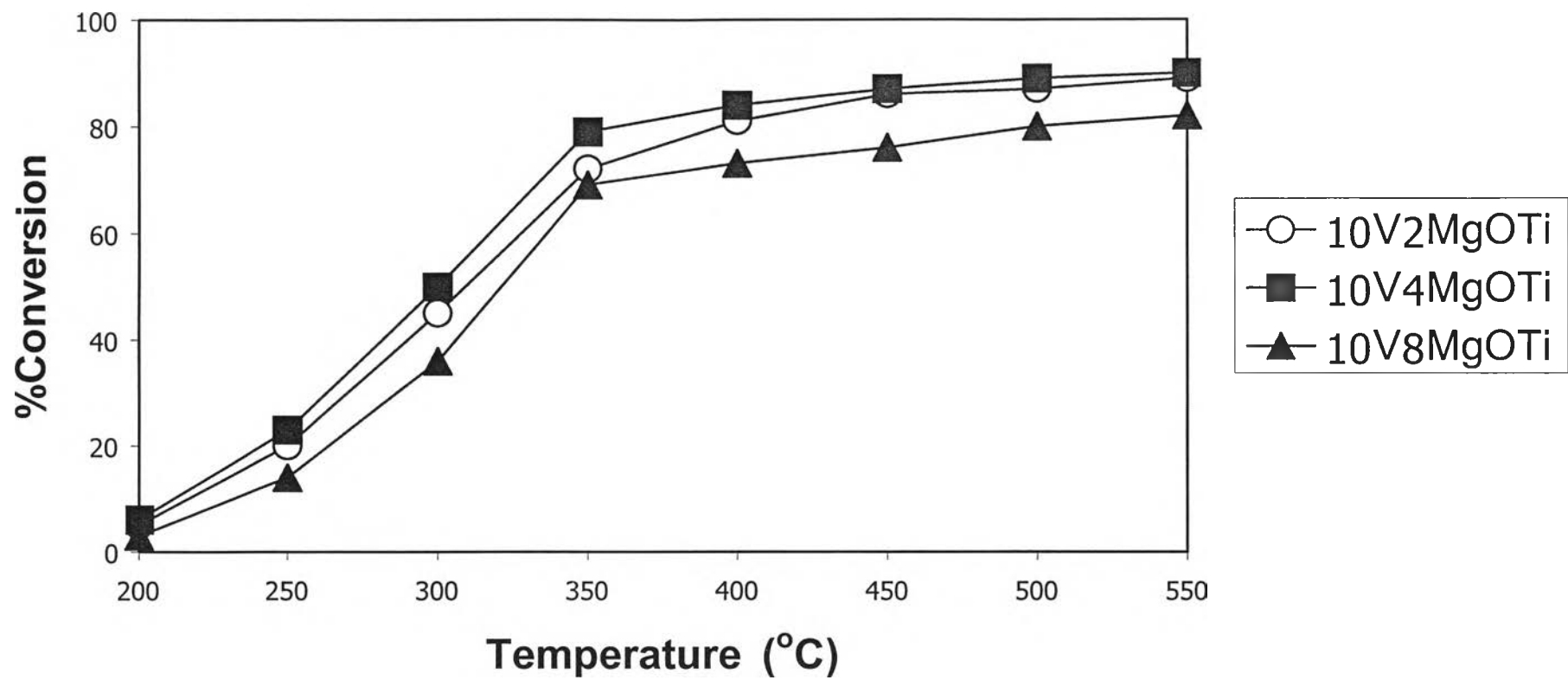


Figure 5.5 The result of phthalic anhydride combustions on VMgOTi with different Mg loading.

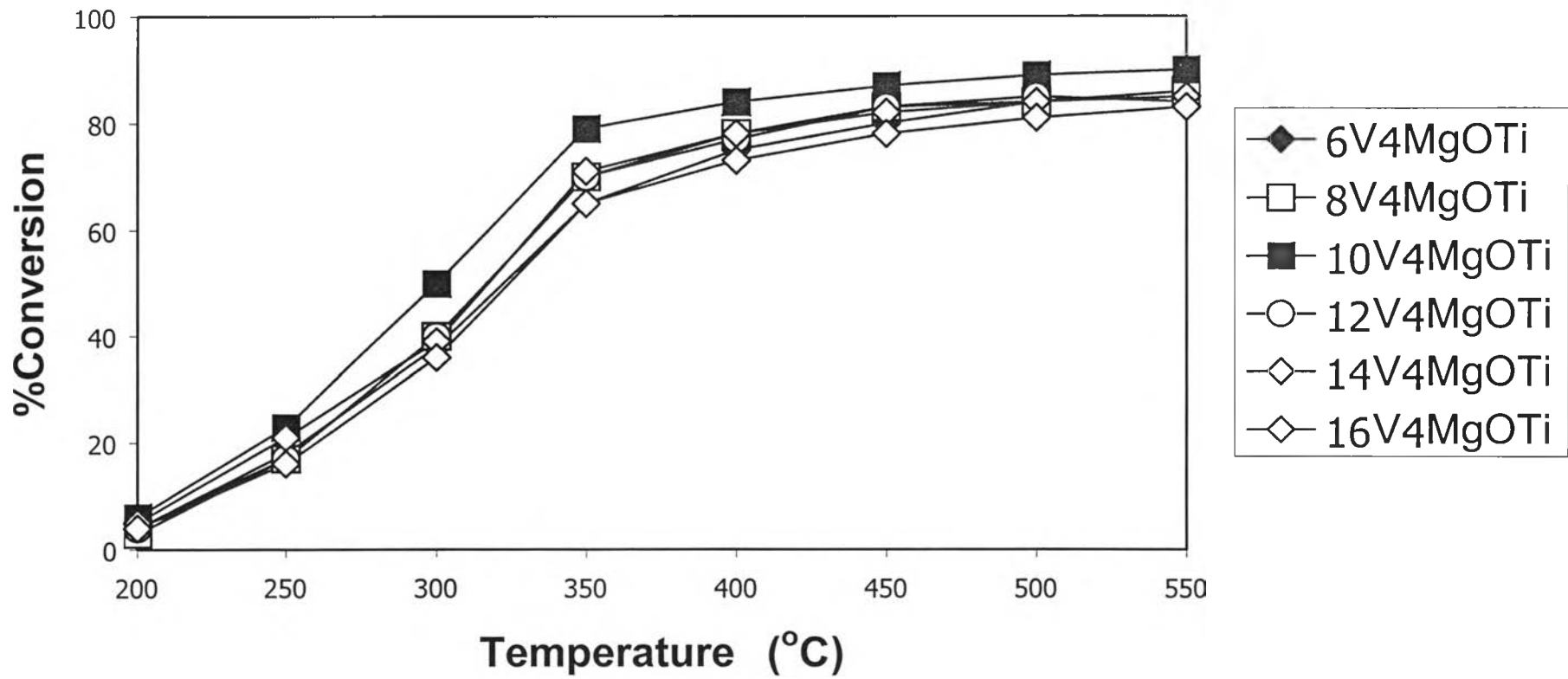


Figure 5.6 The result of phthalic anhydride combustions on VMgOTi with different V loading.

### 5.2.2 Combustion of maleic anhydride.

Maleic anhydride is a by product in the oxidation of *o*-xylene to phthalic anhydride and it is the main product in the oxidation of benzene, butanes and butane. Maleic anhydride is a raw material in chemical industries such as production of alkyd and polyester resins, surface coating, lubricant additives, plasticizers etc. Maleic anhydride has a melting point around 52-54°C and molecular weight is 98.06. The combustion reaction is as follows:

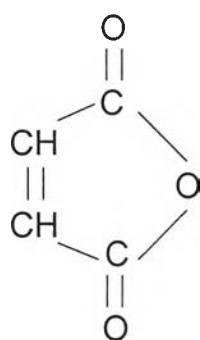
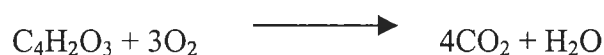


Figure 5.7 The structure of maleic anhydride

#### - Effect of magnesium loading

Figure 5.8 shows the catalytic activity of 10V2MgOTi, 10VTi, 2MgTi, TiO<sub>2</sub> catalysts for maleic anhydride combustion. For 10V2MgOTi catalyst, the conversion of maleic anhydride increased from 3 to 84% at the temperature range of 200 to 400°C and steadily increased until the temperature reached 550°C where the conversion was about 90%. For TiO<sub>2</sub>, the phthalic anhydride conversion enhanced from 3 to 85%. The conversion steadily increased from 2 to 81% at the temperature range of 200 to 550°C for 10Vti catalyst. The conversion steadily increased from 2 to 77% in the same temperature range for 2MgTi catalyst.

2MgTi catalyst shows the maleic anhydride conversion lower than TiO<sub>2</sub> support, indicating that magnesium was not able to catalyze the reaction. Moreover it inhibited the ability to catalyze the reaction of TiO<sub>2</sub>. In the case of loading vanadium on TiO<sub>2</sub> such as 10VTi, it is found that the conversion of maleic anhydride did not improve comparing with unloaded TiO<sub>2</sub>. When loading both vanadium and magnesium into 10V2MgOTi catalyst, the maleic anhydride conversion increased. The conversion was increased about 84% at the temperature range of 200 to 400°C, indicating that magnesium is able to improve the catalytic activity of 10V2MgOTi catalyst. The result revealed that loading magnesium into 10VTi catalyst to form a 10V2MgOTi catalyst can increase the maleic anhydride conversion.

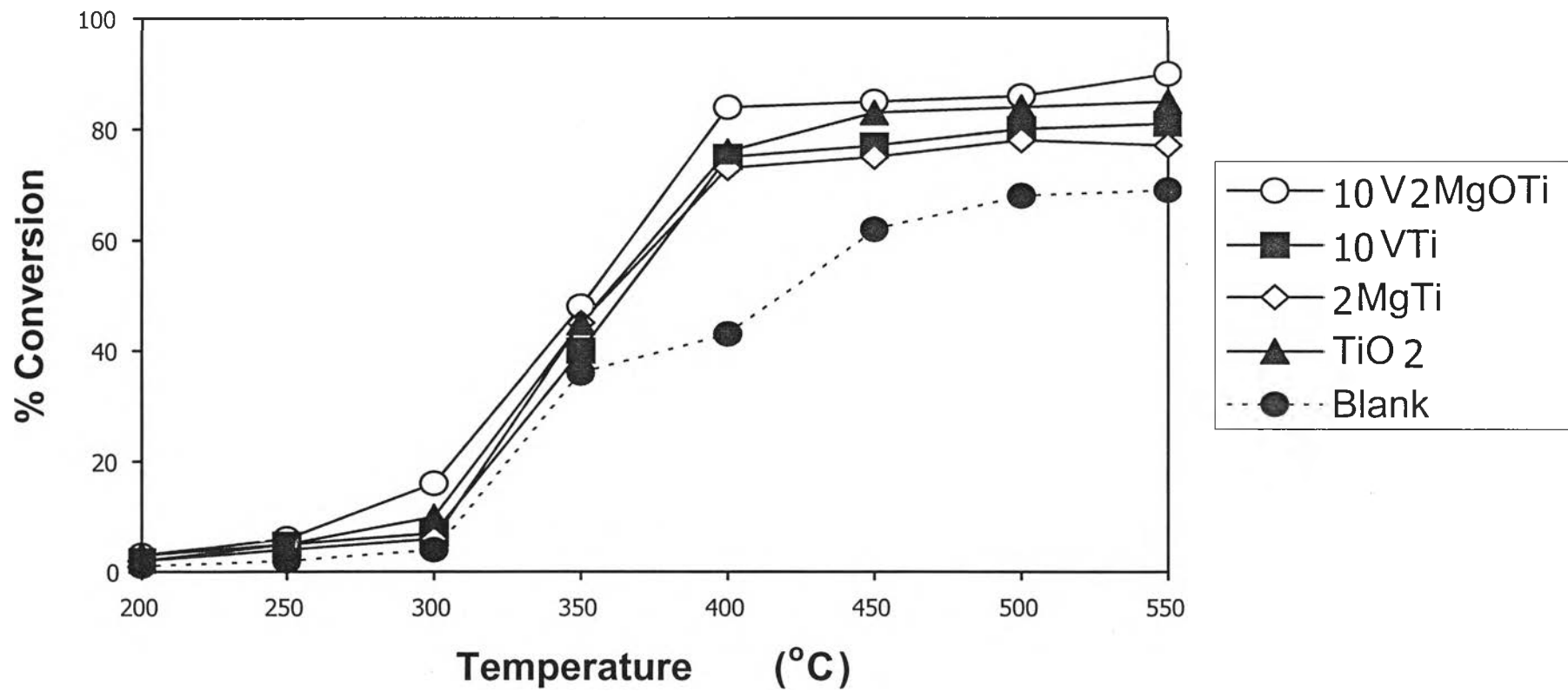


Figure 5.8 The result of maleic anhydride combustions of 10V2MgTi, 10VTi, 2MgTi, TiO<sub>2</sub> and blank.

- *The optimum ratio of V:Mg on catalyst*

- *fixed V wt% with various Mg wt%*

Figure 5.9 shows the maleic anhydride conversions over VMgOTi catalysts that the amount of V is fixed around 10 wt%, while the amount of magnesium is varied to find an optimum amount of magnesium. It is found that 10V4MgOTi shows the best conversion, which increased from 2 to 88% in the range of temperature between 200 to 400°C and steadily raised until the temperature reached 550°C, where the conversion was about 95%. 10V2MgOTi exhibits the conversion from 3 to 90% in the range of temperature at 200 to 550°C and 10V8MgTi catalyst shows the conversion from 2 to 78%. The catalytic activity of these catalysts is in the order of 10V4MgOTi > 10V2MgOTi > 10V8MgOTi.

- *fixed Mg wt% with various V wt%*

Figure 5.10 shows the maleic anhydride conversion on the VMgOTi catalysts. The amount of magnesium is fixed around 4 wt%, while the amount of vanadium oxide is varied to find an optimum amount of vanadium oxide. It was found that 10V4MgOTi shows the best conversion, which increased from 2 to 88% in the temperature range of 200 to 400°C. After that it slightly increased to 95% at 550°C. On the other hand, 6V4MgOTi and 16V4MgTi exhibited almost the same conversion, 2 to 73% in the temperature range of 200 to 550°C. 8V4MgOTi showed the conversion about 2 to 80% and 12V4MgOTi showed the conversion about 2 to 85% in the temperature range of 200 to 550°C. 14V4MgOTi exhibited the conversion about 2 to 90% in the temperature range of 200 to 550°C. The catalytic activity of these catalysts is in the order of 10V4MgOTi > 14V4MgOTi > 12V4MgOTi > 8V4MgOTi > 6V4MgOTi > 16V4MgOTi.



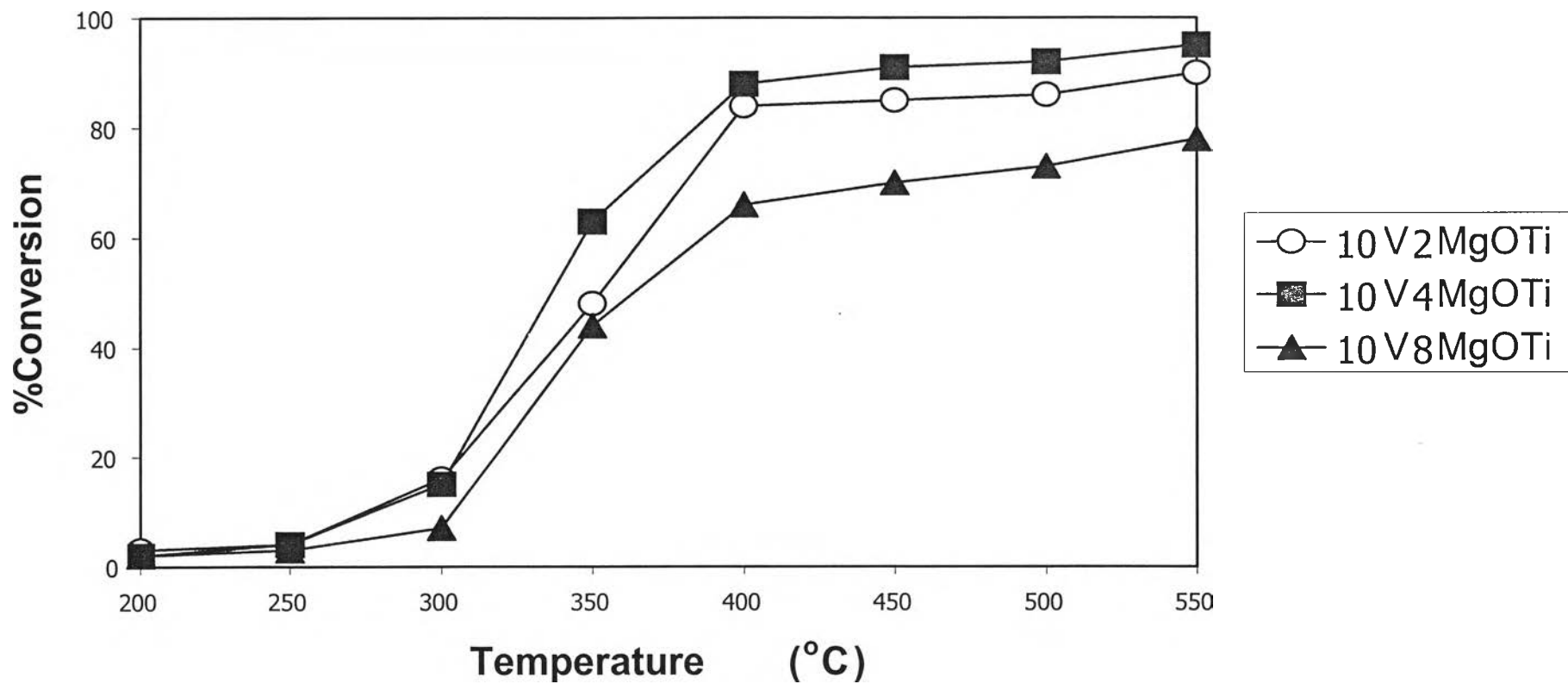


Figure 5.9 The result of maleic anhydride combustions on VMgOTi with different Mg loading.

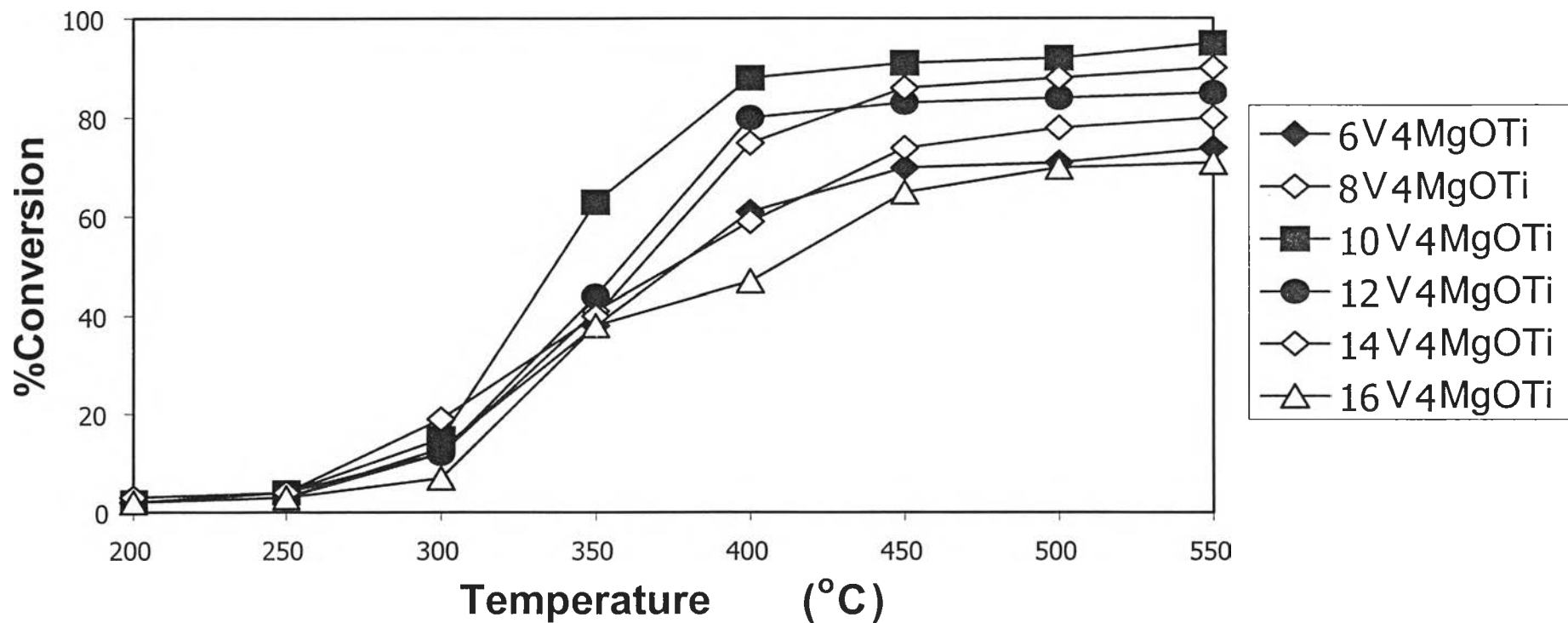


Figure 5.10 The result of maleic anhydride combustions on VMgOTi with different V loading.

The research finds that, the optimum amount of vanadium oxide for phthalic anhydride and maleic anhydride combustion is around 10 wt%. The amount of vanadium loading strongly affects the adsorption of acidic reactant and the catalytic acidity that controlled the catalytic activity. In case of excess vanadium loading, the catalyst acidity increases while the adsorption of acidic reactant decreases that made the catalytic activity decreases, because the ability to adsorb the acidic reactant of magnesium is hidden by vanadium oxide. On the other hand, lean vanadium loading affects the activity of the catalyst to decrease. The catalytic activity decreased because the leanness of active site to react with the anhydride and magnesium is not able to catalyze the reaction by itself.

It should be noted here that, in the case of maleic anhydride combustion, the VMgOTi catalyst does not perform much better than the VTi, MgTi and TiO<sub>2</sub> catalysts as in the case of phthalic anhydride combustion. Phthalic anhydride has the active position to initiate the reaction only at the anhydride ring while the benzene ring is hardly to decompose for maleic anhydride, the combustion can occur at both the anhydride group and the C=C bond. The test to find the initiate reaction position was investigated by using the combustion reaction of benzene and alkyl benzenes such as toluene, ethyl-benzene and acetic acid.

### **5.2.3 Combustion of benzene, toluene, ethyl-benzene and acetic acid.**

#### *- combustion of benzene*

Figure 5.11 represents benzene conversion of blank and 10V2MgOTi catalyst. 10V2MgTi shows the conversion of benzene approaches to zero in the temperature range of 200 to 400°C. After that it rapidly increases to 60% at 550°C. On the other hand, blank test exhibits the conversion of benzene as same as 10V2MgTi catalyst. The main products observed are only CO<sub>2</sub> and H<sub>2</sub>O.

The result in figure 5.11 shows that between 400-500°C 10V2MgOTi gives slightly more benzene conversion than blank, possibly due to better mixing and heat

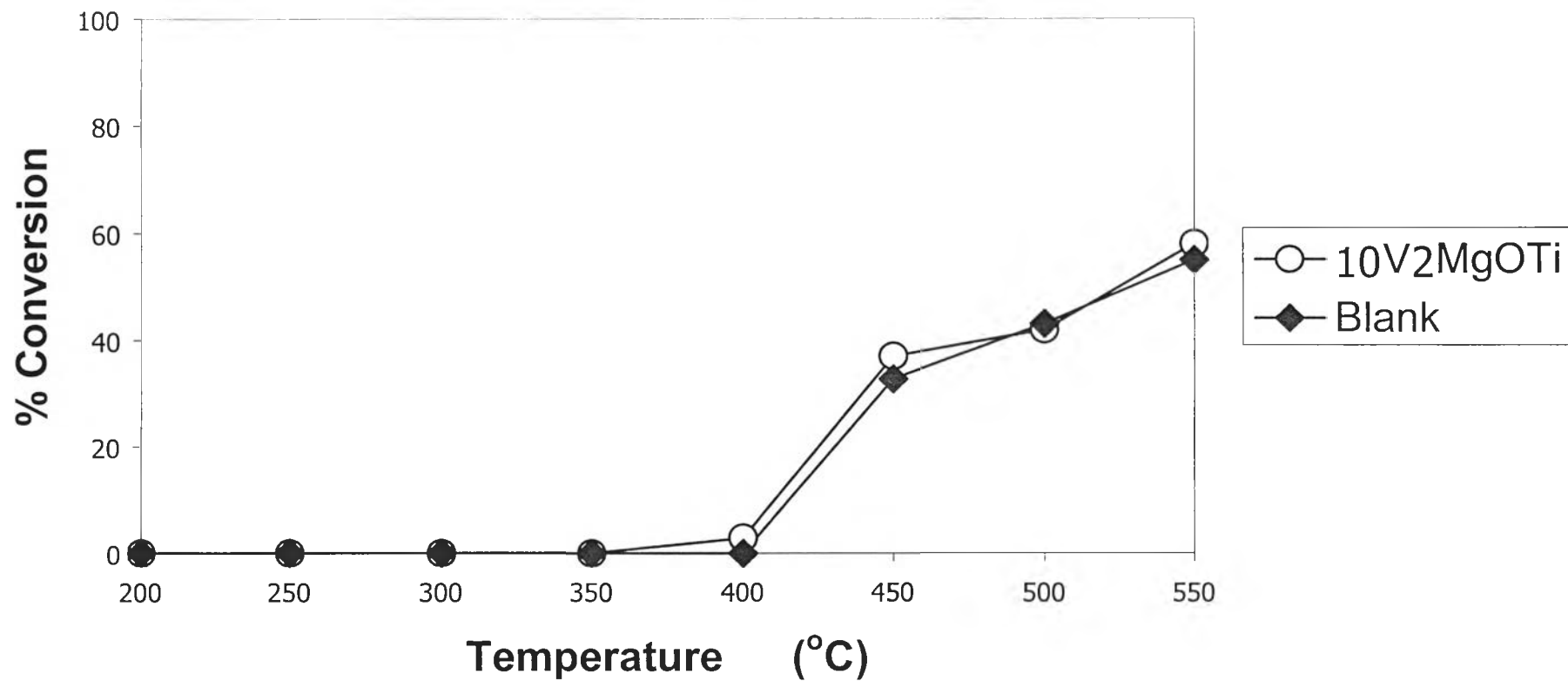


Figure 5.11 The result of benzene combustion of 10V2MgOTi and blank.

transfer when the catalyst is packed. Thus 10V2MgOTi has no capability to activate the benzene ring.

*- Combustion of toluene*

Toluene consists of a benzene ring and a methyl group, CH<sub>3</sub>. Figure 5.12 shows the conversion of toluene approaches to zero in the temperature range of 200 to 400°C. After that it rapidly increases to 60% at 550°C. The main products observed are only CO<sub>2</sub> and H<sub>2</sub>O.

From figures 5.11 and 5.12, the conversion of toluene is similar to the conversion of benzene. Thus the 10V2MgOTi also has no capability to activate to the -CH<sub>3</sub> group of toluene.

*- Combustion of ethylbenzene*

Ethylbenzene consists of a benzene ring and an alkyl group, CH<sub>2</sub>-CH<sub>3</sub>. Theoretically, the presence of a methylene group (CH<sub>2</sub>) in the ethyl group should make ethyl benzene easier to be oxidised than toluene. Figure 5.13 shows the conversion of ethyl-benzene approaches to zero in the temperature range of 200 to 350°C. After that it rapidly increases to 62% at 550°C. The main products observed are only CO<sub>2</sub> and H<sub>2</sub>O.

The conversion of ethylbenzene is also similar to the conversions of benzene and toluene. Thus the 10V2MgOTi does not have capability to activate the methylene group (CH<sub>2</sub>) of the ethyl group.

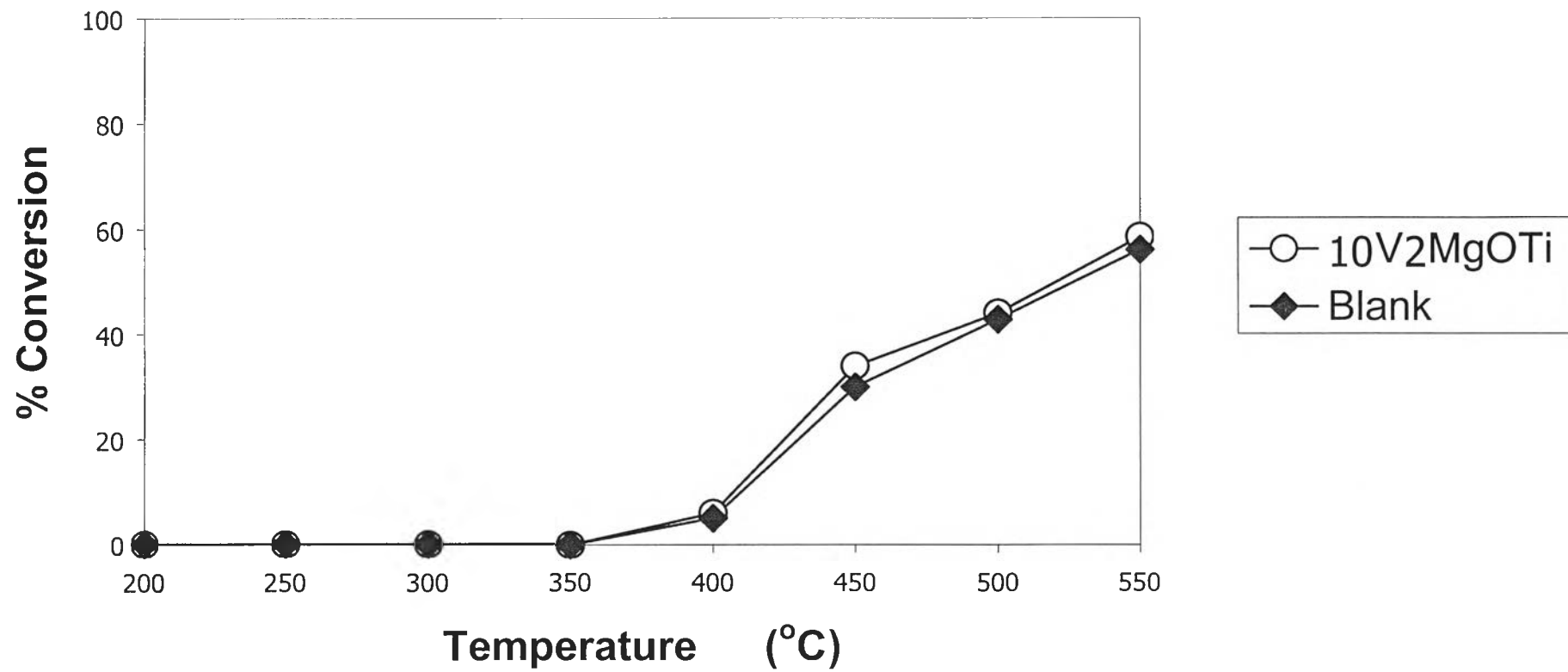


Figure 5.12 The result of toluene combustion of 10V2MgOTi and blank.

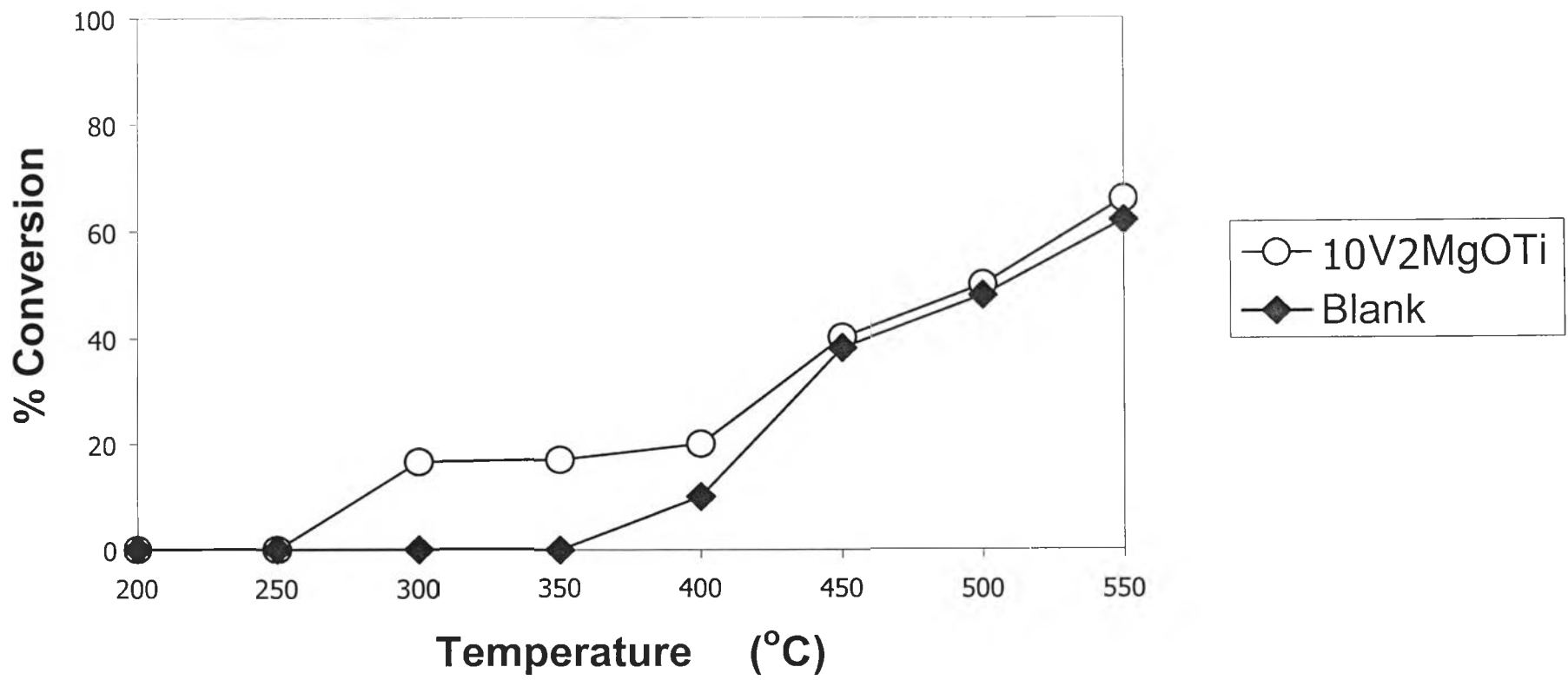


Figure 5.13 The result of ethyl-benzene combustion of 10V2MgOTi and blank.

*- Combustion of acetic acid*

The combustion of benzene, toluene and ethyl-benzene shows that VMgOTi does not activate the benzene ring and the alkyl groups. However, it actively reacts with phthalic anhydride. Therefore, it possibly activates with the carboxyl group. Because of the simple structure of acetic acid, it is used to prove this hypothesis.

Figure 5.14 represents acetic acid conversion of blank, TiO<sub>2</sub> support and VMgOTi catalyst. For 10V2MgOTi catalyst, the conversion of acetic acid increased from 13 to 93% at the temperature range of 200 to 350°C and steadily increased up to nearly 100% when the temperature reached 550°C. On the other hand, TiO<sub>2</sub> and blank, acetic acid conversion enhanced from 12 to 96%. The main products observed are only CO<sub>2</sub> and H<sub>2</sub>O.

10V2MgOTi catalyst shows the best conversion. The catalytic activity of 10V2MgOTi is higher than TiO<sub>2</sub> and blank. Therefore, it can be concluded that 10V2MgOTi can better activate the carboxyl group than the case of blank and TiO<sub>2</sub> support.

It can be seen that the results of combustion of benzene, toluene, ethyl-benzene and acetic acid confirm the above hypothesis.



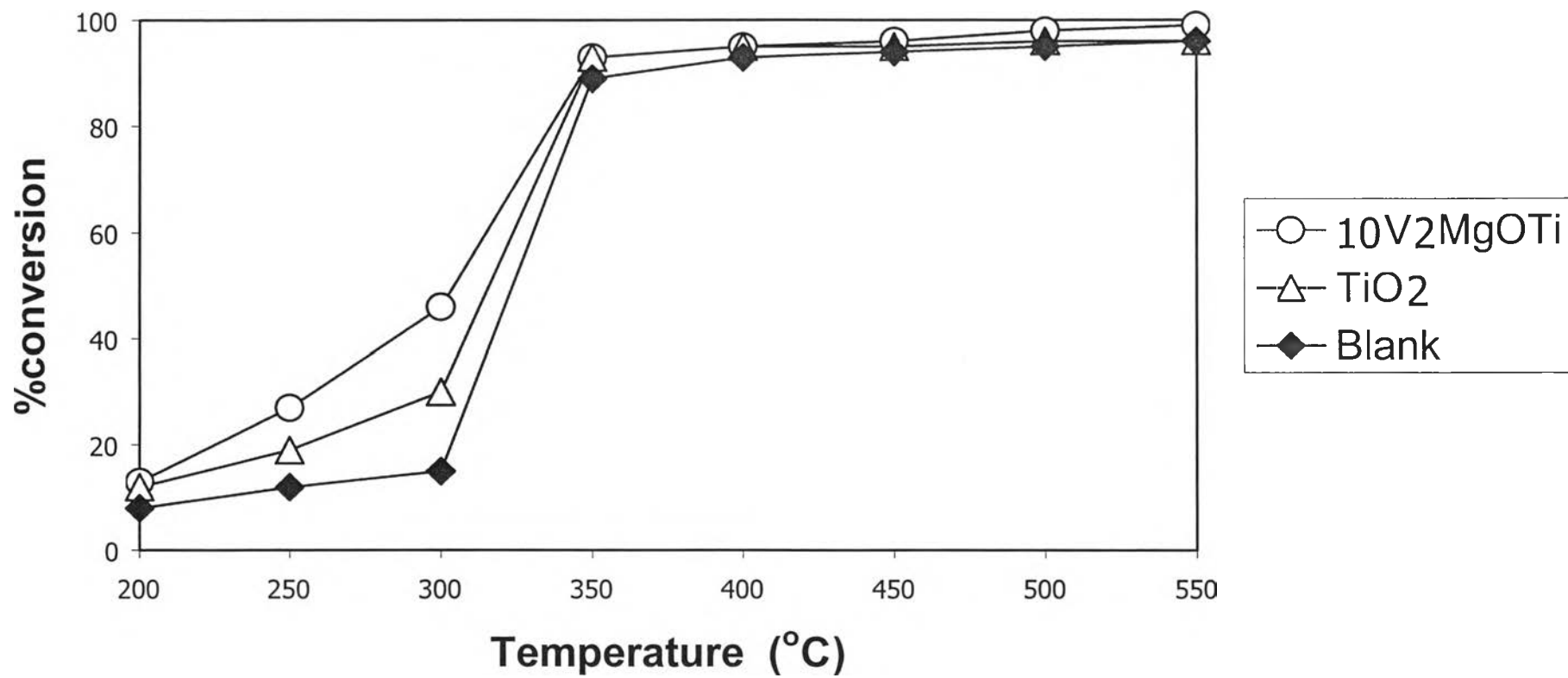


Figure 5.14 The result of acetic acid combustion of 10V2MgOTi, TiO<sub>2</sub> and blank.