

## CHAPTER VI

### RESULTS AND DISCUSSION

The main feature of this research is to enhance the performance of alumina-supported platinum catalyst ( $\text{Pt}/\text{Al}_2\text{O}_3$ ) and titanium oxide-supported platinum catalyst ( $\text{Pt}/\text{TiO}_2$ ) for controlling exhaust emission from conventional petrol engines, which operate close to stoichiometric condition. It is emphasized to the catalyst preparation by varying a calcination temperature in either oxidizing or reducing atmosphere. The catalysts prepared from different technique are tested with a model exhaust gas to study the catalytic activity in the oxidation of CO and  $\text{C}_3\text{H}_8$  including the reduction of NO. This gas mixture is composed of 0.05 vol%NO, 0.30 vol%CO, 0.215 vol% $\text{C}_3\text{H}_8$ , 1.2 vol% $\text{O}_2$  and balanced with He under stoichiometric condition. Besides, the effect of oxygen on the catalytic activity was studied by changing the amount of oxygen from 1.2 vol% $\text{O}_2$  (stoichiometric condition) to 5 vol% (lean-burn condition). As reported by Asavapitchyont [21], platinum was chosen to be a main component catalyst because it could abate CO,  $\text{C}_3\text{H}_8$  and NO simultaneously at stoichiometric condition. The catalytic activity in this study is compared by using “light-off temperature” which is defined as the temperature at which a 50% conversion is reached with respect to the gas being converted [46]. That is to say the lower the light-off temperature, the higher the catalytic activity. The results and discussion are categorized into 6 parts as follows:

- 6.1 Effect of the calcination temperature on the activity of 0.3%Pt/ $\text{Al}_2\text{O}_3$  and 0.3%Pt/ $\text{TiO}_2$  catalysts for NO, CO and  $\text{C}_3\text{H}_8$  removal under stoichiometric condition
- 6.2 Catalyst characterization
- 6.3 Comparison between oxide form and metal form catalysts
- 6.4 Comparison between metal form and SMSI form catalysts
- 6.5 Effect of  $\text{O}_2$  on the activity of 0.3%Pt/ $\text{Al}_2\text{O}_3$  and 0.3%Pt/ $\text{TiO}_2$  catalysts for NO, CO and  $\text{C}_3\text{H}_8$  removal
- 6.6 Discussion

### **6.1 Effect of the calcination temperature on the activity of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> and 0.3%Pt/TiO<sub>2</sub> catalysts for NO, CO and C<sub>3</sub>H<sub>8</sub> removal under stoichiometric condition**

The first experiment of this research is set to study the effect of a calcination temperature on the activity of alumina-supported platinum catalyst (Pt/Al<sub>2</sub>O<sub>3</sub>) and titanium oxide-supported platinum catalyst (Pt/TiO<sub>2</sub>) for CO and C<sub>3</sub>H<sub>8</sub> oxidation and NO reduction. These catalysts were tested in a temperature range 25-500°C under stoichiometric condition.

In this experiment, the catalysts were prepared by varying the calcination temperature at 380°C, 450°C, 500°C, 550°C and 650°C. The two calcination methods were set as follows:

1. calcination in air
2. calcination in a reducing atmosphere (10%H<sub>2</sub>/N<sub>2</sub>)

The effective periods of time for the calcination in air and in a reducing atmosphere are 3 h [13, 23] and 7 h [13, 22, 23], respectively. The preparation details of the different catalysts are summarized in Table 6.1. To accommodate in discussion, these catalysts are also labelled as shown in this table.

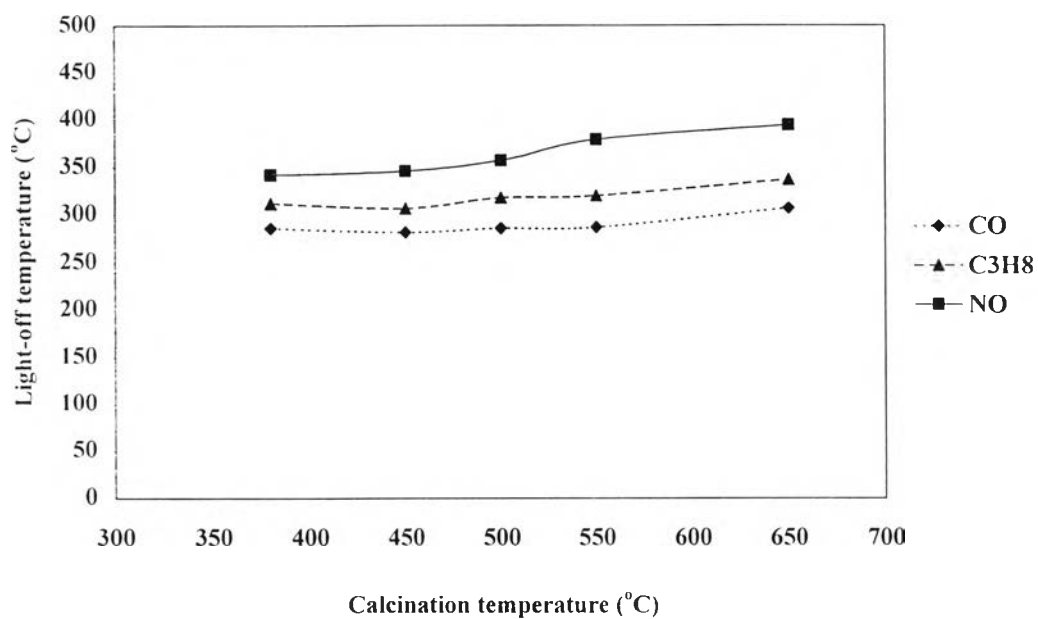
From Table 6.1, these catalysts are divided into 4 groups as follows:

1. CAT.1-CAT.5, 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from calcination in air
2. CAT.6-CAT.10, 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from calcination in a reducing atmosphere
3. CAT.11-CAT.15 and CAT.21, 0.3%Pt/TiO<sub>2</sub> catalysts prepared from calcination in air
4. CAT.16-CAT.20 and CAT.22, 0.3%Pt/TiO<sub>2</sub> catalysts prepared from calcination in a reducing atmosphere

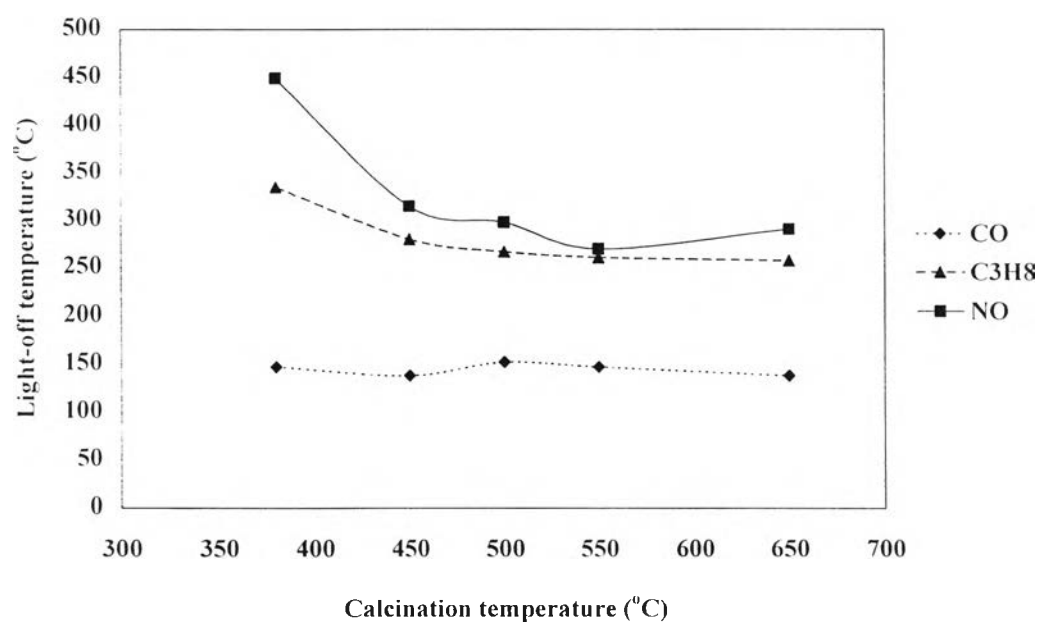
After testing the reaction, the light-off temperatures for NO reduction, CO and C<sub>3</sub>H<sub>8</sub> oxidation are plotted as functions of the calcination temperature to evaluate their catalytic performance.

**Table 6.1** Name of catalyst and preparation condition

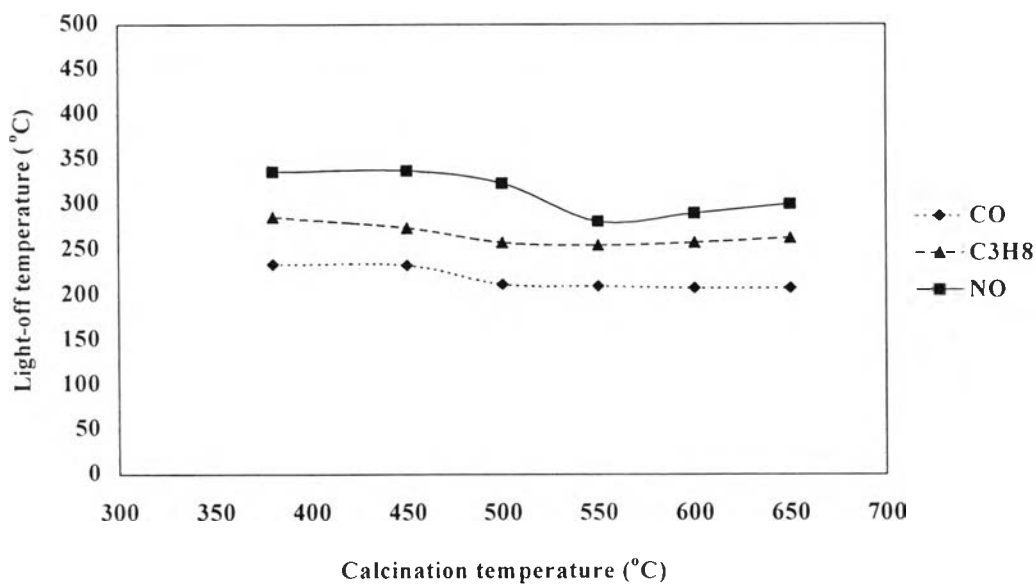
Name	Catalyst composition	Preparation condition		
		Calcination atmosphere	Calcination temperature (°C)	Calcination time (h)
CAT.1	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	air	380	3
CAT.2	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	air	450	3
CAT.3	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	air	500	3
CAT.4	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	air	550	3
CAT.5	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	air	650	3
CAT.6	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	10% H <sub>2</sub> in N <sub>2</sub>	380	7
CAT.7	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	10% H <sub>2</sub> in N <sub>2</sub>	450	7
CAT.8	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	10% H <sub>2</sub> in N <sub>2</sub>	500	7
CAT.9	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	10% H <sub>2</sub> in N <sub>2</sub>	550	7
CAT.10	0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	10% H <sub>2</sub> in N <sub>2</sub>	650	7
CAT.11	0.3%Pt/TiO <sub>2</sub>	air	380	3
CAT.12	0.3%Pt/TiO <sub>2</sub>	air	450	3
CAT.13	0.3%Pt/TiO <sub>2</sub>	air	500	3
CAT.14	0.3%Pt/TiO <sub>2</sub>	air	550	3
CAT.15	0.3%Pt/TiO <sub>2</sub>	air	650	3
CAT.16	0.3%Pt/TiO <sub>2</sub>	10% H <sub>2</sub> in N <sub>2</sub>	380	7
CAT.17	0.3%Pt/TiO <sub>2</sub>	10% H <sub>2</sub> in N <sub>2</sub>	450	7
CAT.18	0.3%Pt/TiO <sub>2</sub>	10% H <sub>2</sub> in N <sub>2</sub>	500	7
CAT.19	0.3%Pt/TiO <sub>2</sub>	10% H <sub>2</sub> in N <sub>2</sub>	550	7
CAT.20	0.3%Pt/TiO <sub>2</sub>	10% H <sub>2</sub> in N <sub>2</sub>	650	7
CAT.21	0.3%Pt/TiO <sub>2</sub>	air	600	3
CAT.22	0.3%Pt/TiO <sub>2</sub>	10% H <sub>2</sub> in N <sub>2</sub>	600	7



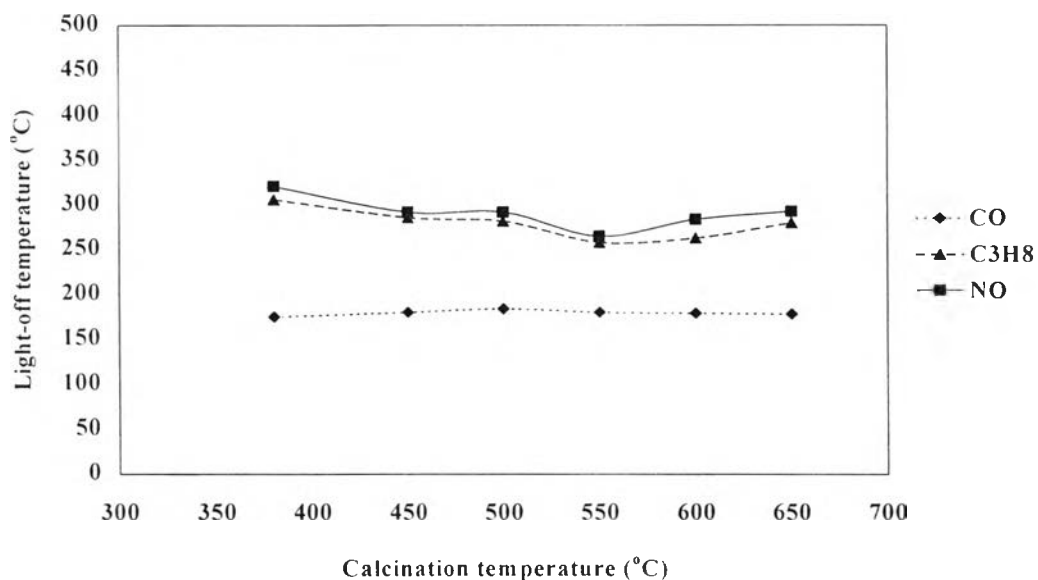
**Figure 6.1** The effect of calcination temperature of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in air on the light-off temperatures of CO, C<sub>3</sub>H<sub>8</sub> and NO under stoichiometric condition



**Figure 6.2** The effect of calcination temperature of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in a reducing atmosphere on the light-off temperatures of CO, C<sub>3</sub>H<sub>8</sub> and NO under stoichiometric condition



**Figure 6.3** The effect of calcination temperature of 0.3%Pt/TiO<sub>2</sub> catalyst calcined in air on the light-off temperatures of CO, C<sub>3</sub>H<sub>8</sub> and NO under stoichiometric condition



**Figure 6.4** The effect of calcination temperature of 0.3%Pt/TiO<sub>2</sub> catalyst calcined in a reducing atmosphere on the light-off temperatures of CO, C<sub>3</sub>H<sub>8</sub> and NO under stoichiometric condition

Figure 6.1 shows the effect of calcination temperature of the 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in air (CAT.1-CAT.5) on NO reduction and CO and C<sub>3</sub>H<sub>8</sub> oxidation. It is found that the light-off temperatures of all the catalysts are almost the same for each reaction. Therefore, for the 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in air, it is concluded that the calcination temperature in range 380°C to 650°C hardly affects the catalytic activity.

The effect of calcination temperature of the 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in a reducing atmosphere (CAT.6-CAT.10) on NO reduction and CO and C<sub>3</sub>H<sub>8</sub> oxidation is illustrated in Figure 6.2. It is clearly observed that the light-off temperatures of all the catalysts are different case of CO oxidation. On the other hand, the light-off temperatures for NO reduction and C<sub>3</sub>H<sub>8</sub> oxidation decrease with the increase of calcination temperature when the temperature is below 550°C. When the calcination temperature is above 550°C, these light-off temperatures are almost constant with increasing calcination temperature. For the 0.3 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in a reducing atmosphere, the suitable calcination temperature at which the light-off temperature for all reactions is minimized is 550°C.

Figure 6.3 represents the relationship between the light-off temperature for NO reduction and CO and C<sub>3</sub>H<sub>8</sub> oxidation and the calcination temperature of the 0.3%Pt/TiO<sub>2</sub> catalyst calcined in air (CAT.11-CAT.15 and CAT.21). The same tendency as of those observed in Figure 6.2 was found. It is, however, noted that these light-off temperatures for CO oxidation are almost constant when the calcination temperatures are in range between 380°C and 500°C. Therefore, the optimum calcination temperature in this case is 550°C.

The effect of calcination temperature of the 0.3%Pt/TiO<sub>2</sub> catalyst calcined in a reducing atmosphere (CAT.16-CAT.20 and CAT.22) on NO reduction and CO and C<sub>3</sub>H<sub>8</sub> oxidation is investigated as shown in Figure 6.4. The optimum calcination temperature is 550°C in case of NO reduction and C<sub>3</sub>H<sub>8</sub> oxidation. On the other hand, the light-off temperatures for CO oxidation are rather constant for all catalysts.

From the above results, it is noted that most catalysts prepared from the calcination temperature of 550°C, except Pt/Al<sub>2</sub>O<sub>3</sub> which was calcined in air, give the lowest light-off temperature for the three reactions, i.e., NO reduction, CO and C<sub>3</sub>H<sub>8</sub> oxidation. Therefore, the catalyst prepared at 550°C will be considered in the next section.

## 6.2 Catalyst characterization

### 6.2.1 X-ray Diffraction

X-ray Diffraction is a technique, which identifies the crystal structure by using X-ray radiation. In case of  $\text{Al}_2\text{O}_3$ , the XRD spectrum of pure  $\text{Al}_2\text{O}_3$  is shown in Figure 6.5. It is shown that 2 theta of  $\text{Al}_2\text{O}_3$  is similar to gamma- $\text{Al}_2\text{O}_3$  reported by Inoue *et al* [47]. Figures 6.6 and 6.7 show the XRD spectrum of fresh 0.3%Pt/ $\text{Al}_2\text{O}_3$  catalysts calcined in air and calcined in reducing atmosphere, respectively. It is observed that the 2 theta range from  $10^\circ$  to  $80^\circ$  of all fresh 0.3%Pt/ $\text{Al}_2\text{O}_3$  catalysts is similar to that of pure  $\text{Al}_2\text{O}_3$ . It is concluded that  $\text{Al}_2\text{O}_3$  of both fresh 0.3%Pt/ $\text{Al}_2\text{O}_3$  catalysts is gamma phase.

The XRD spectrum of pure  $\text{TiO}_2$  is illustrated in Figure 6.8. In the 2 theta range from  $20^\circ$  to  $60^\circ$  five peaks are observed:  $25.2^\circ$ ,  $38.5^\circ$ ,  $48.0^\circ$ ,  $53.9^\circ$  and  $55.2^\circ$  in consistence with reported by Sopyan *et al* [48]. No other peaks except those attributed to anatase were observed. These observations show that, within the detection limits of measurement, the XRD pattern consisted of only anatase. Figures 6.9 and 6.10 show the XRD spectrum of fresh 0.3%Pt/ $\text{TiO}_2$  catalysts calcined in air and calcined in a reducing atmosphere, respectively. It can be seen that XRD spectrum of both fresh 0.3%Pt/ $\text{TiO}_2$  catalysts is the same as that of pure  $\text{TiO}_2$ . It is concluded that  $\text{TiO}_2$  of both fresh 0.3%Pt/ $\text{TiO}_2$  catalysts is anatase phase.

Moreover, it can be seen that Pt peak cannot be detected on 0.3%Pt/ $\text{Al}_2\text{O}_3$  and 0.3%Pt/ $\text{TiO}_2$  catalysts as shown in Figure 6.6, 6.7, 6.9 and 6.10, respectively. It means that the amount of Pt on 0.3%Pt/ $\text{Al}_2\text{O}_3$  and 0.3%Pt/ $\text{TiO}_2$  surface may be too small to be determined by XRD.



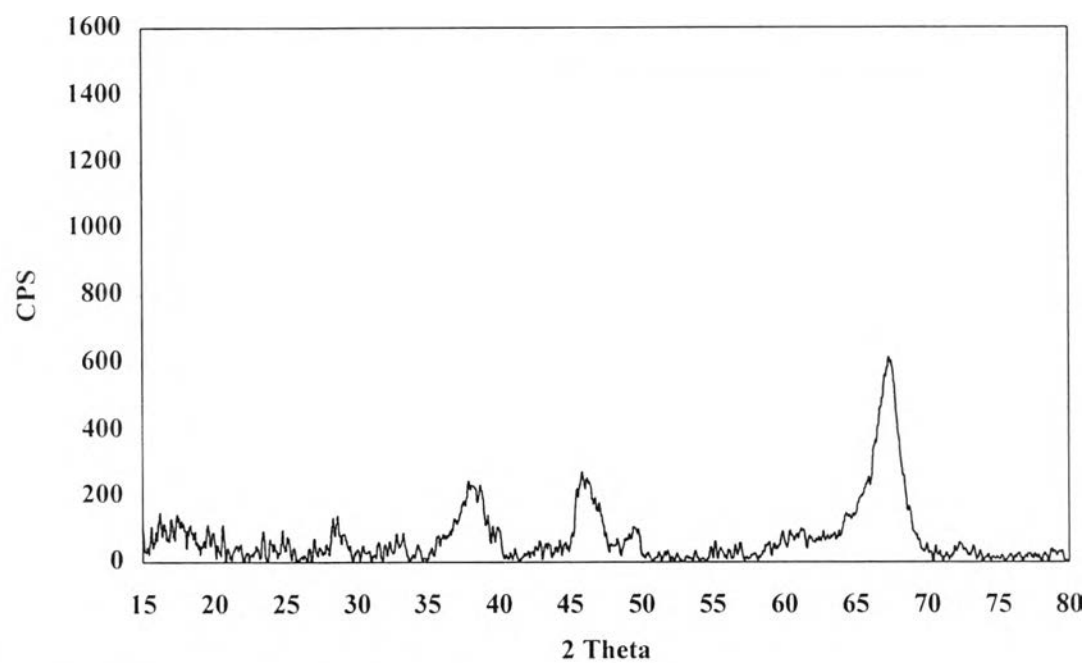


Figure 6.5 X-ray diffraction pattern of pure Al<sub>2</sub>O<sub>3</sub>

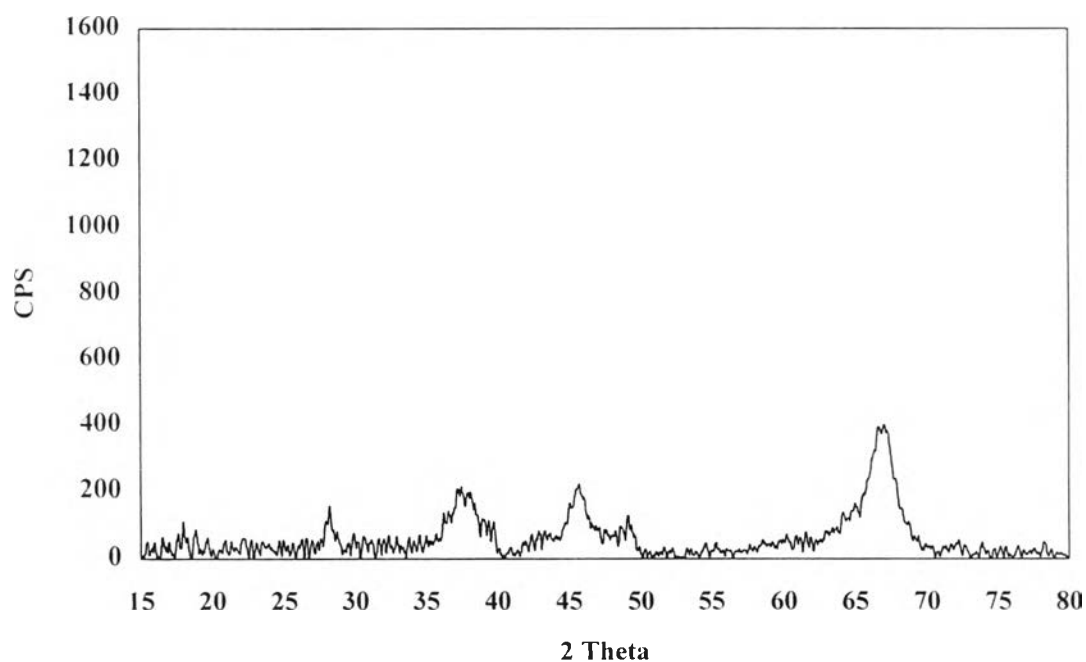
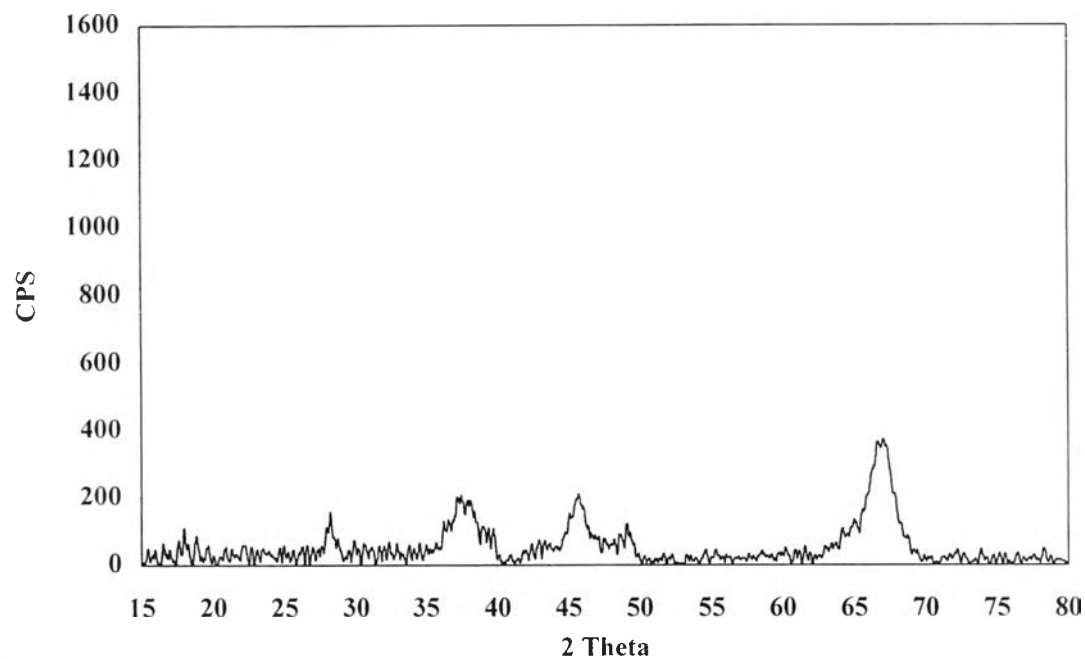
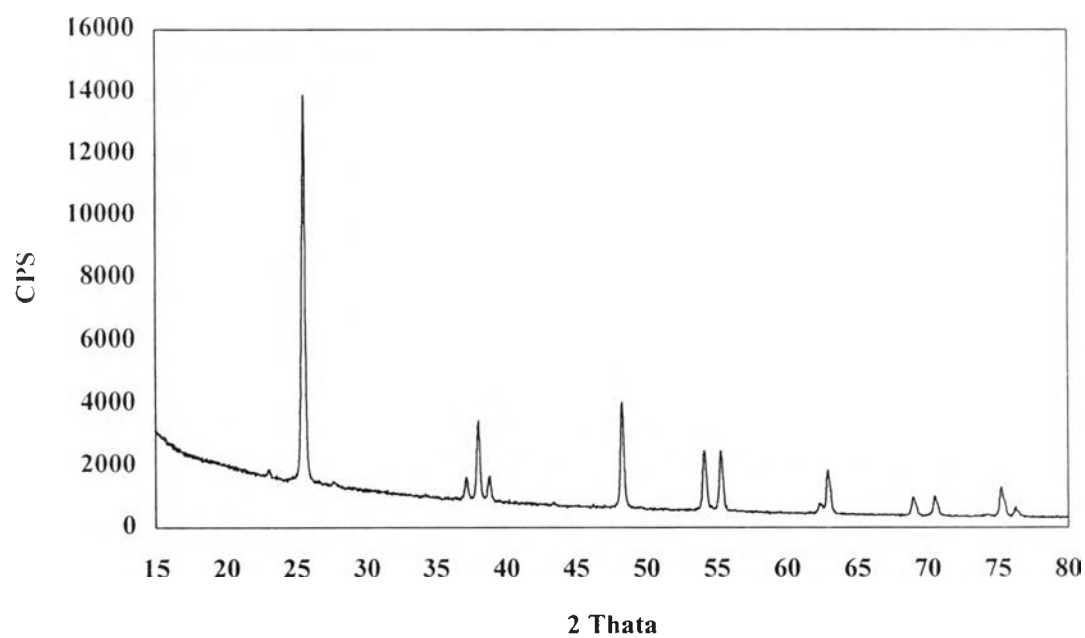


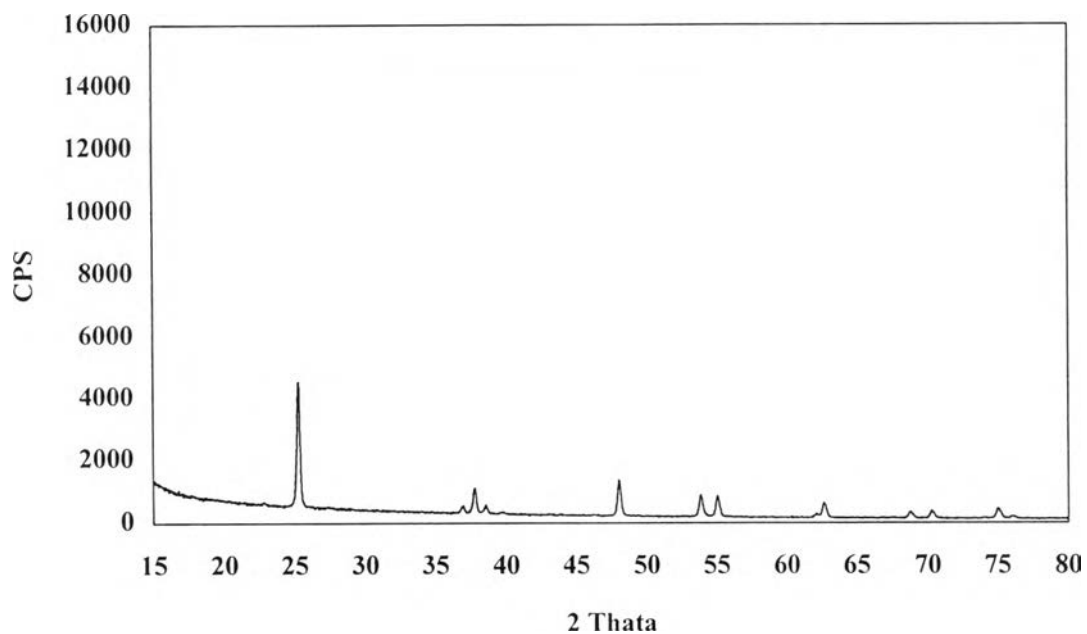
Figure 6.6 X-ray diffraction pattern of fresh 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in air at 550°C



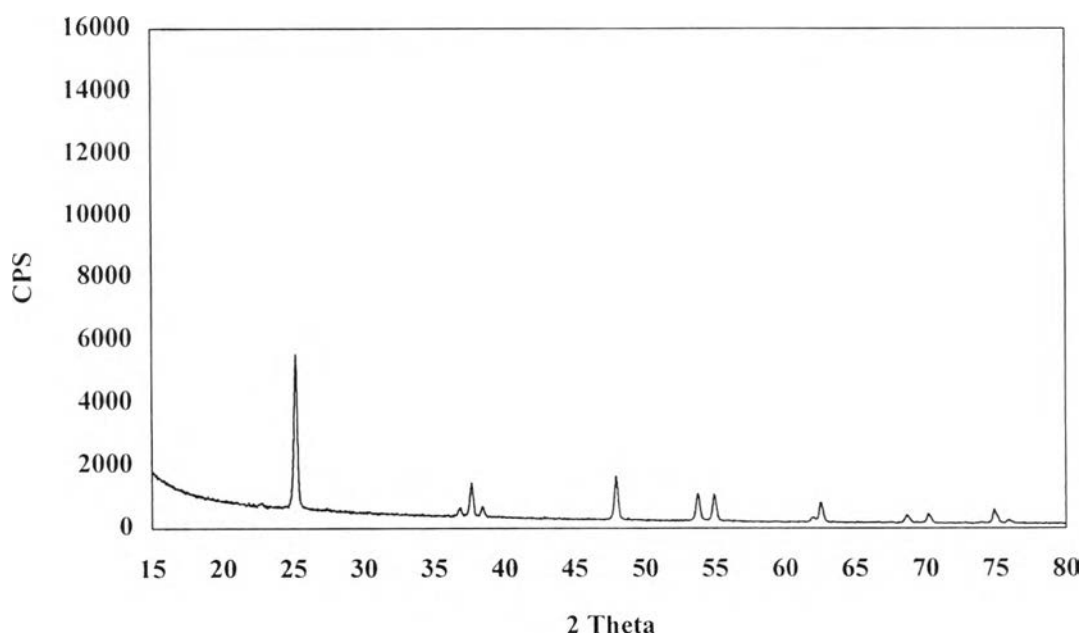
**Figure 6.7** X-ray diffraction pattern of fresh 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst calcined in a reducing atmosphere at 550°C



**Figure 6.8** X-ray diffraction pattern of pure TiO<sub>2</sub>



**Figure 6.9** X-ray diffraction pattern of fresh 0.3%Pt/TiO<sub>2</sub> catalyst calcined in air at 550°C



**Figure 6.10** X-ray diffraction pattern of fresh 0.3%Pt/TiO<sub>2</sub> catalyst calcined in a reducing atmosphere at 550°C

### 6.2.2 The metal active site and BET surface area measurement

**Table 6.2** The metal active site and BET surface area of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> and 0.3%Pt/TiO<sub>2</sub> prepared from a different calcination method

Name	Metal active site ( $\times 10^{18}$ molecule/g cat)	BET surface area (m <sup>2</sup> /g cat)
CAT.1	5.88	270.69
CAT.2	7.89	259.27
CAT.3	10.19	217.76
CAT.4	5.49	209.44
CAT.5	5.54	198.91
CAT.6	4.63	241.28
CAT.7	6.71	234.15
CAT.8	8.43	196.32
CAT.9	4.77	190.74
CAT.10	4.72	166.81
CAT.11	3.37	4.78
CAT.12	3.49	4.74
CAT.13	3.69	4.59
CAT.14	4.44	3.94
CAT.15	3.75	3.74
CAT.16	3.25	4.14
CAT.17	3.42	4.08
CAT.18	3.54	4.11
CAT.19	3.89	3.83
CAT.20	3.57	3.61
CAT.21	4.15	3.85
CAT.22	3.72	6.74
Al <sub>2</sub> O <sub>3</sub>	-	342.45
TiO <sub>2</sub>	-	11.88

Table 6.2 shows BET surface area and the amount of metal active sites measured by CO chemisorption technique. It can be observed that the BET surface area of all alumina supported platinum catalysts (CAT.1-CAT.10) shown in this table is in the range from 166.81 m<sup>2</sup>/g cat to 270.69 m<sup>2</sup>/g cat, while that of pure alumina shown in Table 6.2 is about 342.45 m<sup>2</sup>/g cat. These results could be explained that the pore of alumina is plugged by the loaded Pt [49]. It is also seen that the BET surface area will be decreased when the catalyst is calcined at higher temperature which this result correspond with the result reported by Ozawa [50]. Chang [51] found that treatment at high temperature in hydrogen atmosphere can cause both sintering and changing in particle size and morphology called SMSI for dispersed metal. Moreover, the catalyst prepared in air give higher BET surface area than that prepared in a reducing atmosphere at the same calcination temperature. For an alumina support, it can be therefore concluded that the catalyst calcined at high temperature gives the lower BET surface area than that calcined at low temperature in both calcination methods (in air and in a reducing atmosphere). In case of a titanium oxide support, all catalysts (CAT.11-CAT.20) show a very low BET surface area, because the BET surface area of a pure titanium oxide is generally low. Hence, the BET surface area of these catalysts appears rather a little change to be approximately 3-5 m<sup>2</sup>/g cat.

The metal active site measured by CO chemisorption technique is also considered. It is found that the catalyst prepared in a reducing atmosphere shows the lower metal active site than that prepared in air at the same calcination temperature for both Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/TiO<sub>2</sub> catalysts. It is speculated that the calcination in a reducing atmosphere at high temperature may possibly lead to SMSI phenomenon, suppression of H<sub>2</sub> and CO chemisorption, for catalysts. The consequence of this interaction is a suppression of H<sub>2</sub> and CO chemisorption of the supported metals but they usually do not lost their catalytic activity [52]. The evidence of SMSI was suggested to be able to occur on the reduction of VIII group metals supported on reducible oxides (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) at high temperature [53]. Tauster [54] reported that SMSI phenomenon for supported

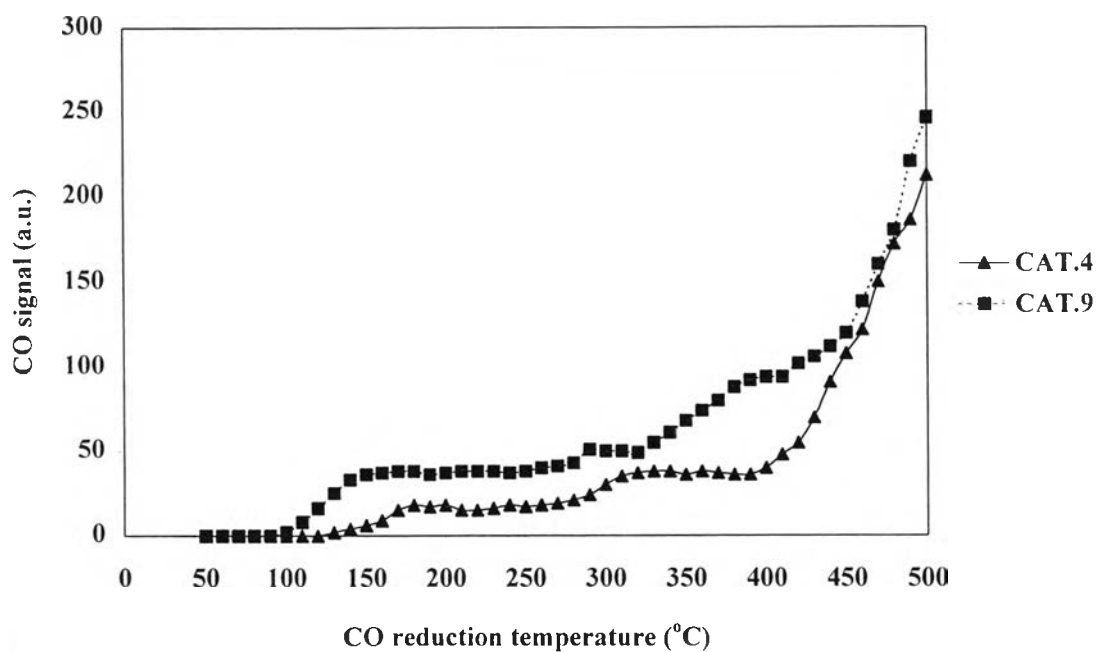
metallic catalysts comes from a reduction at elevated temperature which reduces the cations of the support to an oxidation state lower than its original state.

### 6.2.3 Temperature programmed reduction of carbon monoxide (CO-TPR)

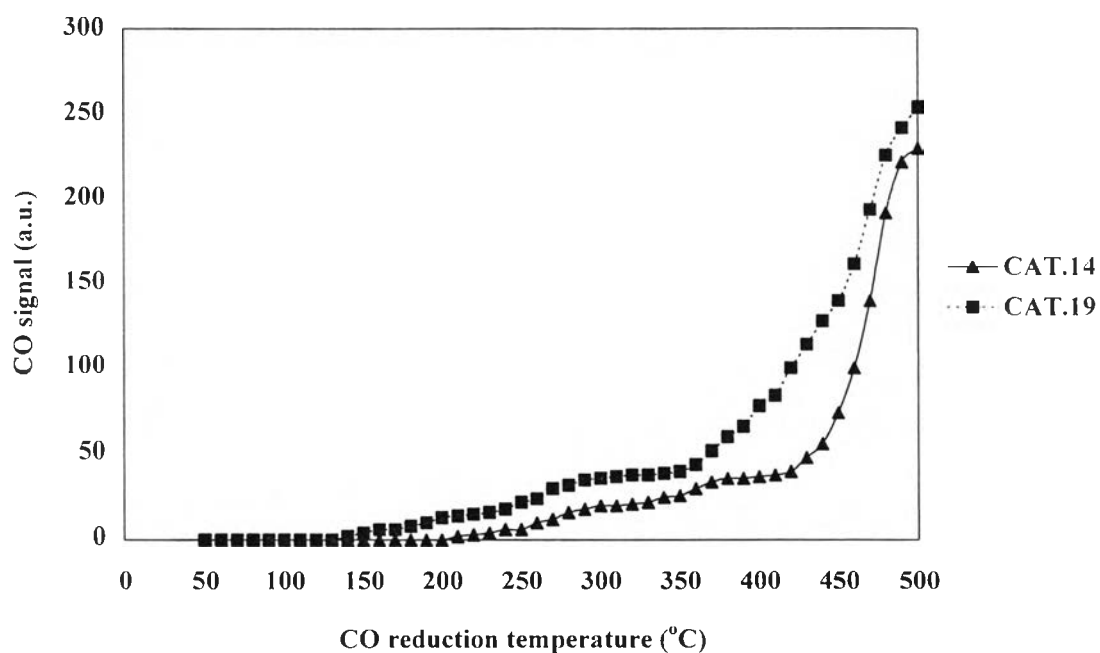
In heterogeneous reaction system, it has catalysts as active phase. Hence, the reactions could be on their active sites only. The important steps in heterogeneous reaction, especially on surface catalyst, are adsorption and desorption of reactant and product, respectively. There are two main reactions for a redox reaction, i.e., oxidation and reduction reactions. Thereby, the competitive of reactant could be induced. Currently, there are several techniques used to study the catalytic surface. The temperature programmed technique is one of those methods. The temperature programmed reduction technique could be also used to interpret the phenomenon on the catalyst surface. The provided technique could explain the behavior of absorbed oxygen strength over catalytic surface [22]. This procedure is described in chapter IV; Figures 6.11 and 6.12 show TPR profiles of CO consumption of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> and 0.3%Pt/TiO<sub>2</sub>, respectively. It is observed that the CO uptake profiles of both catalysts are of the same pattern in each support type, however, their desorption temperature commence at the different temperature. These results can be indicated that the strength of absorbed O<sub>2</sub> on the catalytic surface influence on the initial temperature of CO uptake. On the other hand, if the strength of absorbed O<sub>2</sub> is stronger, the CO uptake is commenced at high temperature. From Figures 6.11 and 6.12, the order of the initial temperature of CO uptake is shown as:

$$\text{CAT.9} < \text{CAT.4} \text{ and } \text{CAT.19} < \text{CAT.14}$$

It means that the catalyst calcined in air can more strongly adsorb oxygen than that calcined in a reducing atmosphere for both the support types.



**Figure 6.11** The temperature programmed reduction profiles of CO consumption on 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> calcined in air and in a reducing atmosphere



**Figure 6.12** The temperature programmed reduction profiles of CO consumption on 0.3%Pt/TiO<sub>2</sub> calcined in air and in a reducing atmosphere

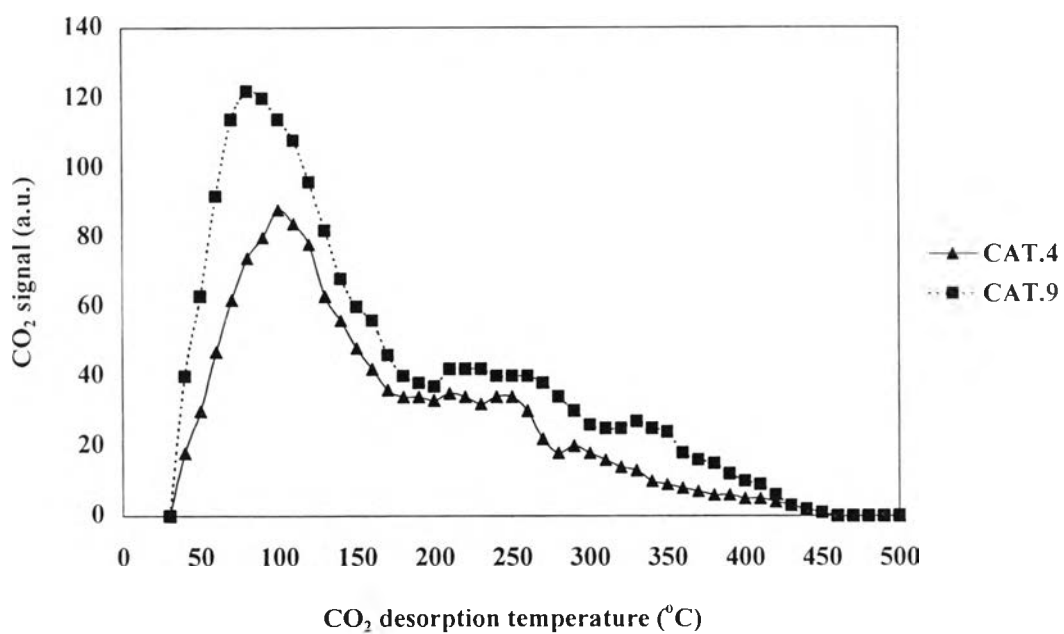
#### 6.2.4 Temperature programmed desorption of carbon dioxide (CO<sub>2</sub>-TPD)

The TPD technique applied to the catalysts used in this work can give information regarding the strength of carbon dioxide adsorption, which is defined as the temperature at maximum carbon dioxide desorption.

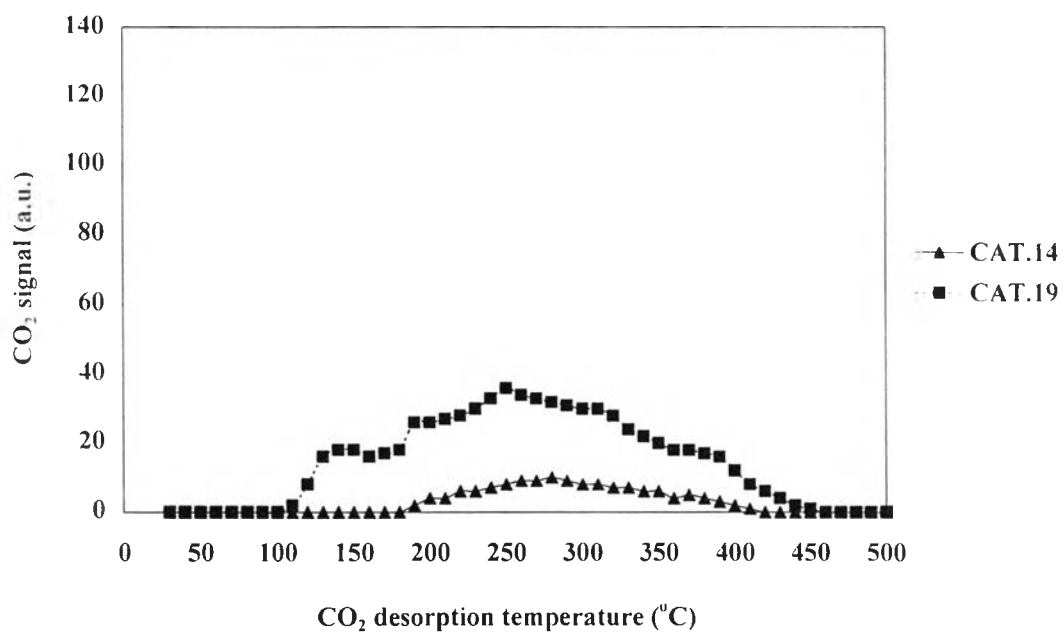
Based on the mechanism of contact catalysis, desorption of the reaction product from the catalyst surface is an important step. When the reaction products are strongly adsorbed on the catalyst surface, the prevention of the reactions from reaching the catalyst surface will be generated [55]. Therefore, the activity of a catalyst depends on its ability to desorb the reaction products from its surface.

Figures 6.13 and 6.14 show CO<sub>2</sub>-TPD profiles of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> and 0.3%Pt/TiO<sub>2</sub>, respectively. It is found that for both the support types, the catalyst calcined in air gives higher temperature at maximum carbon dioxide desorption than that calcined in a reducing atmosphere. Hence, it may be envisaged that the catalyst calcined in a reducing atmosphere has the lower carbon dioxide adsorption strength of the two catalysts. The basicity is proportional to the concentration of CO<sub>2</sub> desorption [56].





**Figure 6.13** The temperature programmed desorption profiles of CO<sub>2</sub> on 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> calcined in air and in a reducing atmosphere



**Figure 6.14** The temperature programmed desorption profiles of CO<sub>2</sub> on 0.3%Pt/TiO<sub>2</sub> calcined in air and in a reducing atmosphere

From the characterization results which compose of CO<sub>2</sub>-TPD, CO-TPR, BET surface area and CO-adsorption, it is clearly seen that the catalyst calcined in air differ from those calcined in a reducing atmosphere. Therefore, the effect of catalyst preparation condition on activity for removing exhaust gas is considered in the next section.

Generally, the calcination in air could make platinum become platinum oxide, especially PtO<sub>2</sub> which is the most stable form [57]. On the other hand, the calcination in a reducing atmosphere differs from this above calcination. It could make platinum become clean surface because hydrogen is a potential reductant for reducing the catalyst surface. Besides, if the calcination temperature is high enough, the SMSI phenomenon may be occurred.

Basically, common to all proposed SMSI mechanism is the high-temperature reduction of the support by hydrogen [31] and suppression of H<sub>2</sub> and CO chemisorption of the supported metals [53]. It is therefore concluded that the catalyst calcined in the reducing atmosphere at 550°C is in SMSI form as already discussed in section 6.2.

Investigation of the surface of both catalysts before testing the catalytic activity. There are two different forms; i.e., metal form and oxide form.

Many researchers found that NO reduction depends on several parameters, e.g., reaction condition [4,15], type of support [12,14,25,27] and reductant [3,15,28,30]. The catalyst surface is another effective parameter. Burch and Watling [58] found that nitrogen monoxide decomposition occurs rapidly over platinum sites. Hence, the effect of SMSI phenomenon on the catalytic activity may be not clear, if the two catalysts are directly compared. The catalyst is then prepared by a new method to eliminate the influence upon the catalytic surface.

The oxidized catalyst will be reduced in H<sub>2</sub> at 500°C for 1 h before testing the catalytic activity to change into metal form catalyst. It is expected that this reduced catalyst is not in SMSI form, since metal active site and BET surface area are similar to those of oxidized catalyst, these results are shown in Table 6.3.

**Table 6.3** The metal active site and BET surface area of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> and 0.3%Pt/TiO<sub>2</sub> in three form

Catalyst composition	Catalyst form	Metal active site ( $\times 10^{18}$ molecule/g cat)	BET surface area (m <sup>2</sup> /g cat)
0.3%Pt/Al <sub>2</sub> O <sub>3</sub>	oxide	5.49	209.44
	metal	5.47	290.26
	SMSI	4.77	190.74
0.3%Pt/TiO <sub>2</sub>	oxide	4.44	3.94
	metal	4.41	3.91
	SMSI	3.89	3.83

Note: calcination temperature 550°C

The following terms used herein are defined as:

- Oxide form catalyst represents the catalyst, which is calcined in air
- Metal form catalyst represents the catalyst, which is calcined in air and then reduced in H<sub>2</sub>
- SMSI form catalyst represents catalyst, which is calcined in a reducing atmosphere

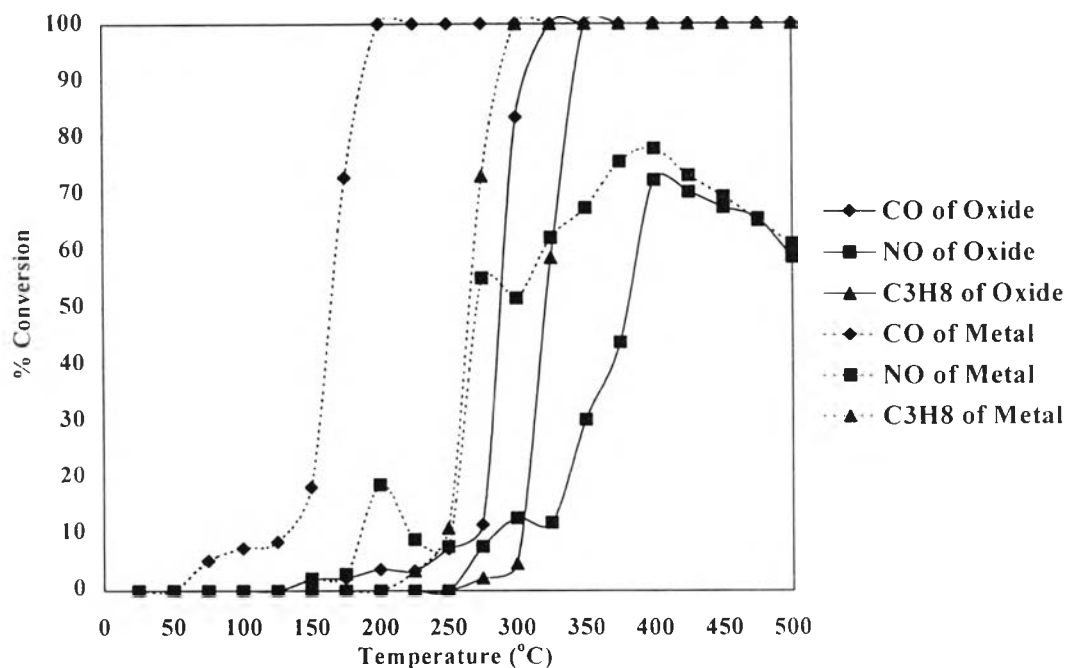
The next section will discuss about tested activity of these catalysts. The oxide form and metal form catalysts are compared to observe the influence of the catalytic surface on the catalytic activity in the section 6.3. The metal form and SMSI form catalyst are compared to investigate the effect of SMSI phenomenon in section 6.4.

### 6.3 Comparison between oxide form and metal form catalysts

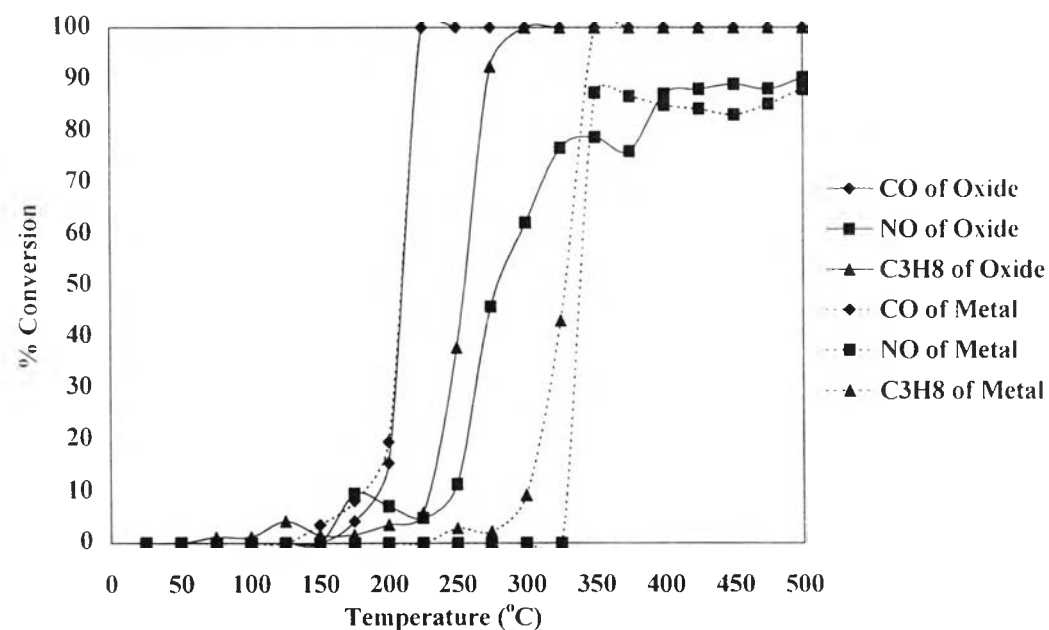
This section is divided into 2 parts; the first part mentions  $\text{Al}_2\text{O}_3$  supported platinum catalyst while the second one reports  $\text{TiO}_2$  supported platinum catalyst.

In case of  $\text{Al}_2\text{O}_3$  supported platinum catalyst, CO,  $\text{C}_3\text{H}_8$  and NO conversions of 0.3%Pt/ $\text{Al}_2\text{O}_3$  in different forms (oxide and metal) are demonstrated in Figure 6.15. It is observed that the metal form catalyst makes all conversions start at lower temperature but the conversion profiles have similar tendency. It can be therefore concluded that the metal form catalyst gives higher activity for removing the exhaust gas than the oxide form catalyst under stoichiometric condition.

In case of  $\text{TiO}_2$  supported platinum catalyst, CO,  $\text{C}_3\text{H}_8$  and NO conversions of 0.3%Pt/ $\text{TiO}_2$  in different forms (oxide and metal) are illustrated in Figure 6.16. It is found that the metal form and the oxide form catalyst give similar CO conversion. For  $\text{C}_3\text{H}_8$  and NO conversion, it is observed that the oxide form catalyst gives higher conversion than the metal form catalyst. Therefore, it can be concluded that the oxide form catalyst gives higher activity for removing the exhaust gas than the metal form catalyst under stoichiometric condition.



**Figure 6.15** Comparison of CO, C<sub>3</sub>H<sub>8</sub> and NO conversion of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst between oxide form and metal form catalysts under stoichiometric condition



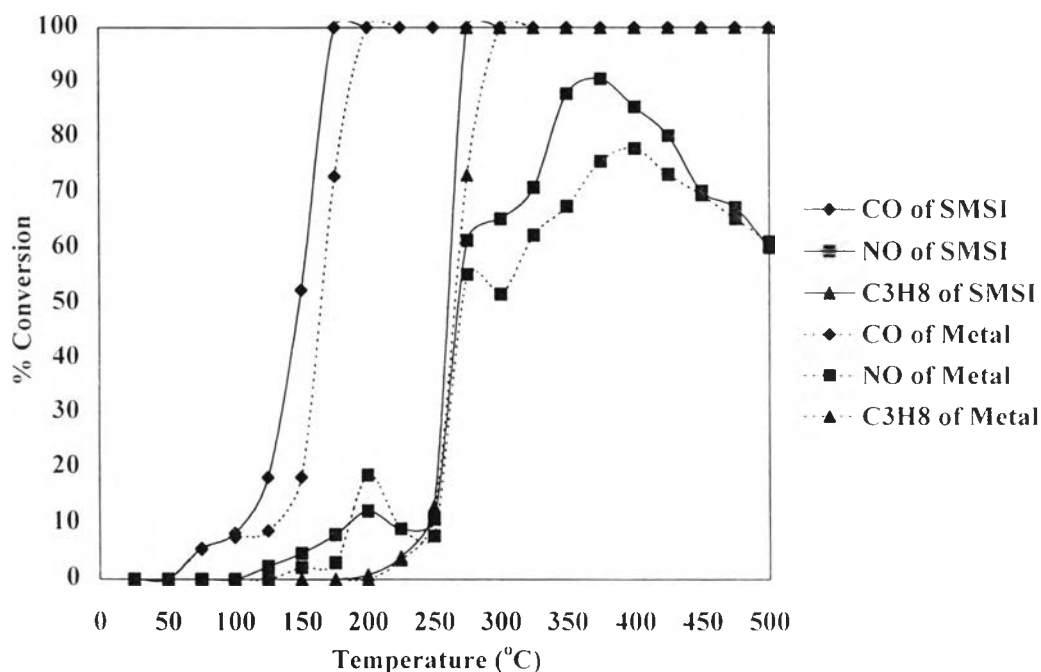
**Figure 6.16** Comparison of CO, C<sub>3</sub>H<sub>8</sub> and NO conversion of 0.3%Pt/TiO<sub>2</sub> catalyst between oxide form and metal form catalysts under stoichiometric condition

#### 6.4 Comparison between metal form and SMSI form catalysts

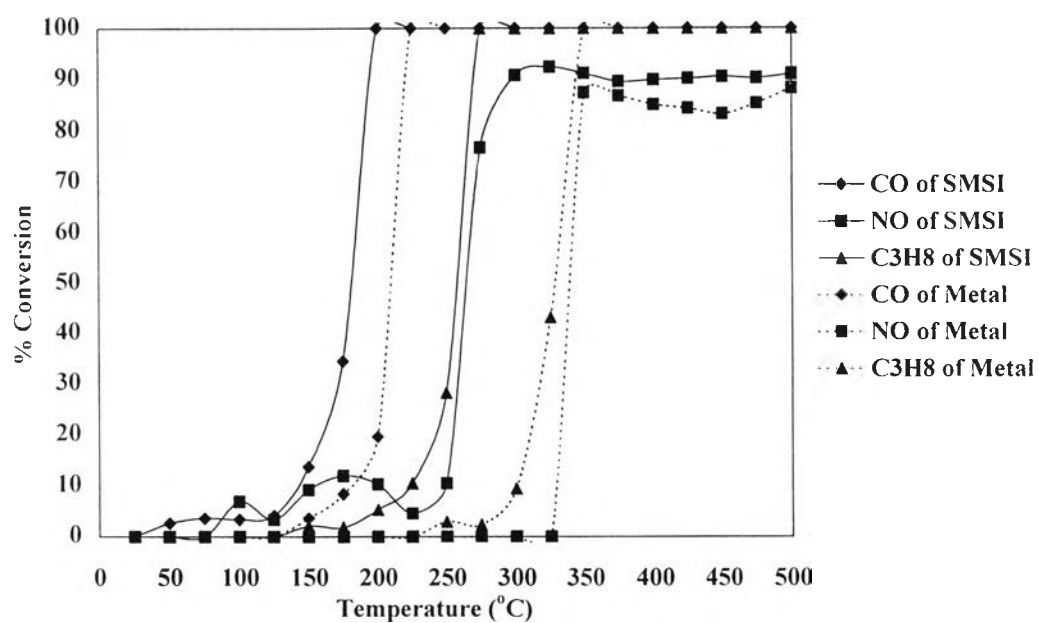
This section is divided into 2 parts;  $\text{Al}_2\text{O}_3$  supported platinum catalyst and  $\text{TiO}_2$  supported platinum catalyst.

In case that the catalyst was prepared by using  $\text{Al}_2\text{O}_3$  support, it is observed that the SMSI form catalyst gives a little higher CO,  $\text{C}_3\text{H}_8$  and NO conversions than the metal form catalyst does as illustrated in Figure 6.17.

In case of  $\text{TiO}_2$  supported platinum catalysts, CO,  $\text{C}_3\text{H}_8$  and NO conversions examined on the SMSI form catalyst are obviously greater than those observed on the metal form catalyst as shown in Figure 6.18.



**Figure 6.17** Comparison of CO,  $\text{C}_3\text{H}_8$  and NO conversions of 0.3%Pt/ $\text{Al}_2\text{O}_3$  catalyst between metal form and SMSI form catalyst under stoichiometric condition



**Figure 6.18** Comparison of CO, C<sub>3</sub>H<sub>8</sub> and NO conversions of 0.3%Pt/TiO<sub>2</sub> catalyst between metal form and SMSI form catalyst, under stoichiometric condition

## **6.5 Effect of O<sub>2</sub> on the activity of 0.3% Pt/Al<sub>2</sub>O<sub>3</sub> and 0.3% Pt/TiO<sub>2</sub> catalysts for NO, CO and C<sub>3</sub>H<sub>8</sub> removal**

The catalytic activity for the oxidation of CO and C<sub>3</sub>H<sub>8</sub> including the reduction of NO was investigated under oxidizing condition. The gas mixture is composed of 0.05 vol%NO, 0.30 vol%CO, 0.215 vol%C<sub>3</sub>H<sub>8</sub>, 5 vol%O<sub>2</sub> and balanced with He. Under this oxidizing condition in the lean-burn exhaust gas, the 3-way catalyst will act as an oxidation catalyst controlling CO and HC emissions, but the conversion of the NO<sub>x</sub> emissions falls to very low levels [4].

This section is divided into 2 parts as follows:

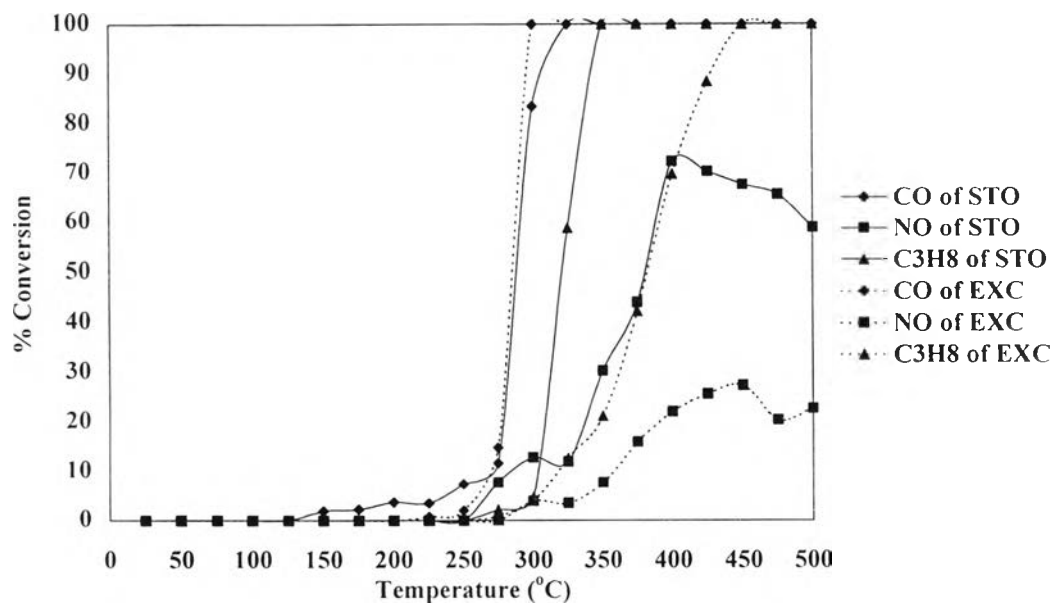
6.5.1 Comparison of the catalytic activities under different operating conditions. i.e., the stoichiometric and lean-burn conditions

6.5.2 Comparison of the catalytic activities measured on the oxide form, metal form and SMSI form catalysts

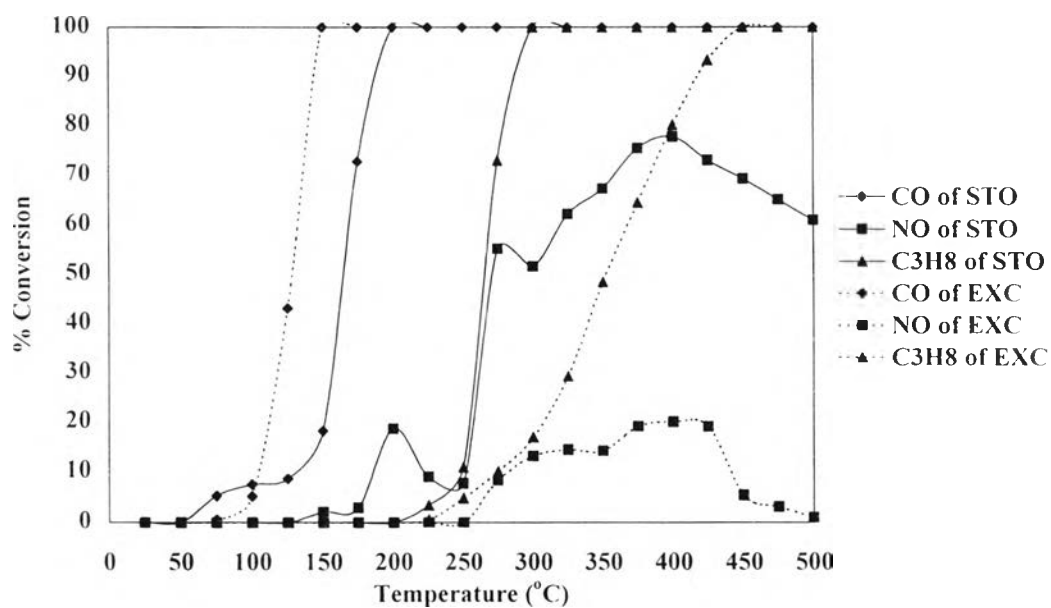
### **6.5.1 Comparison of the catalytic activities under different operating conditions, i.e., the stoichiometric and lean-burn conditions**

The catalytic performances for simultaneously removing CO, C<sub>3</sub>H<sub>8</sub> and NO under stoichiometric and lean-burn conditions are compared as shown in Figures 6.19-6.24. It is observed that all catalysts tested under lean-burn condition give the lower light-off temperature of CO oxidation than those tested under stoichiometric condition. On the other hand, in case of C<sub>3</sub>H<sub>8</sub> oxidation and NO reduction, the catalysts operated under stoichiometric condition show the better performance than those observed under the lean-burn condition. C<sub>3</sub>H<sub>8</sub> conversions slowly increase with temperature under lean-burn condition but they sharply increase with temperature under stoichiometric condition. Additionally, the catalysts tested under lean-burn condition show a very little NO conversion. particularly, for all 0.3%Pt/TiO<sub>2</sub> catalysts. no NO conversion is shown.

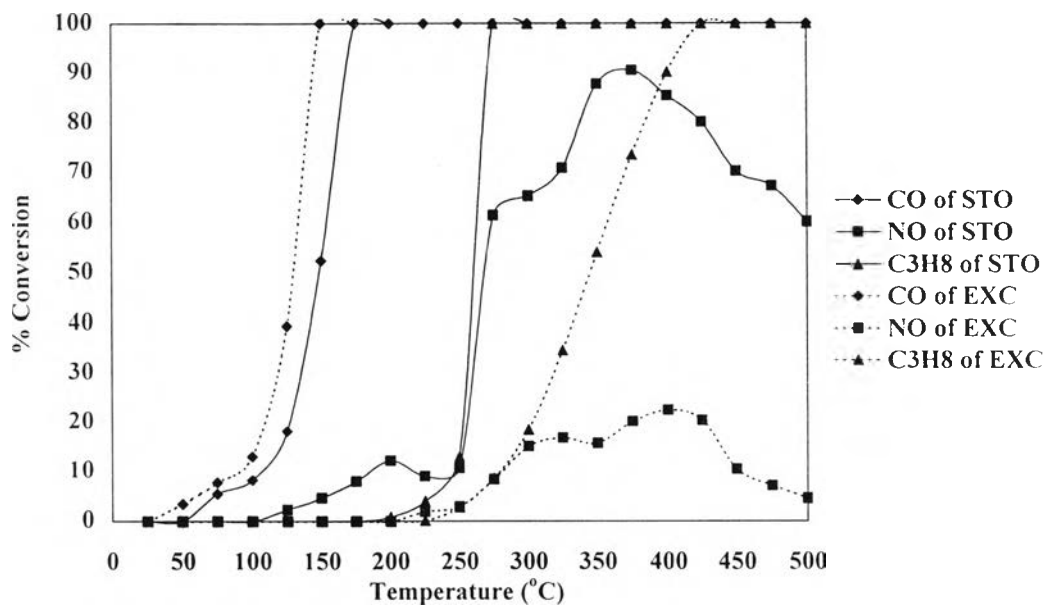




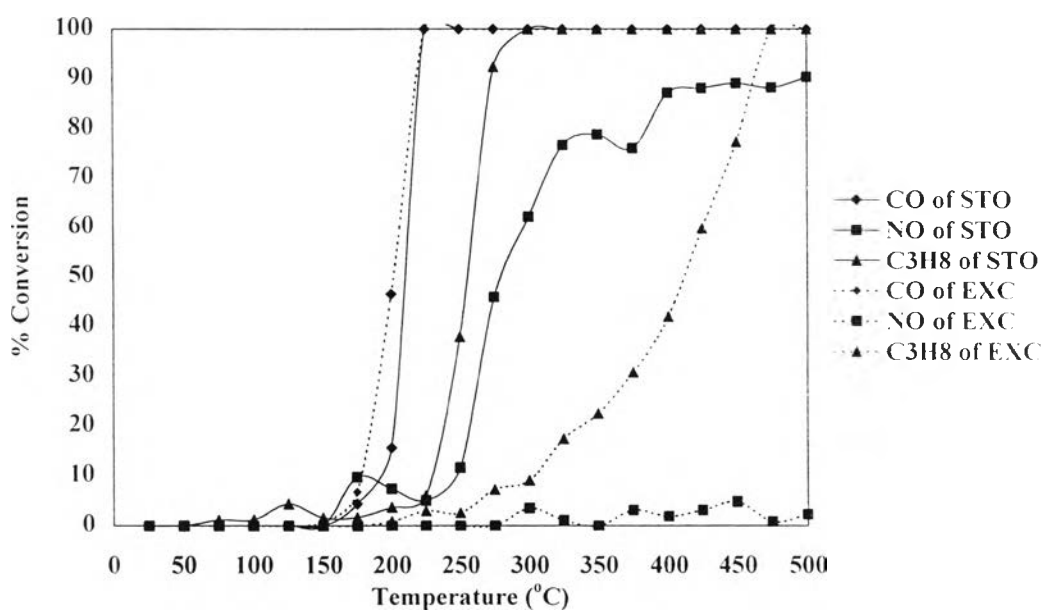
**Figure 6.19** Comparison of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> in oxide form under lean-burn and stoichiometric conditions (STO = stoichiometric condition, EXC = lean-burn condition)



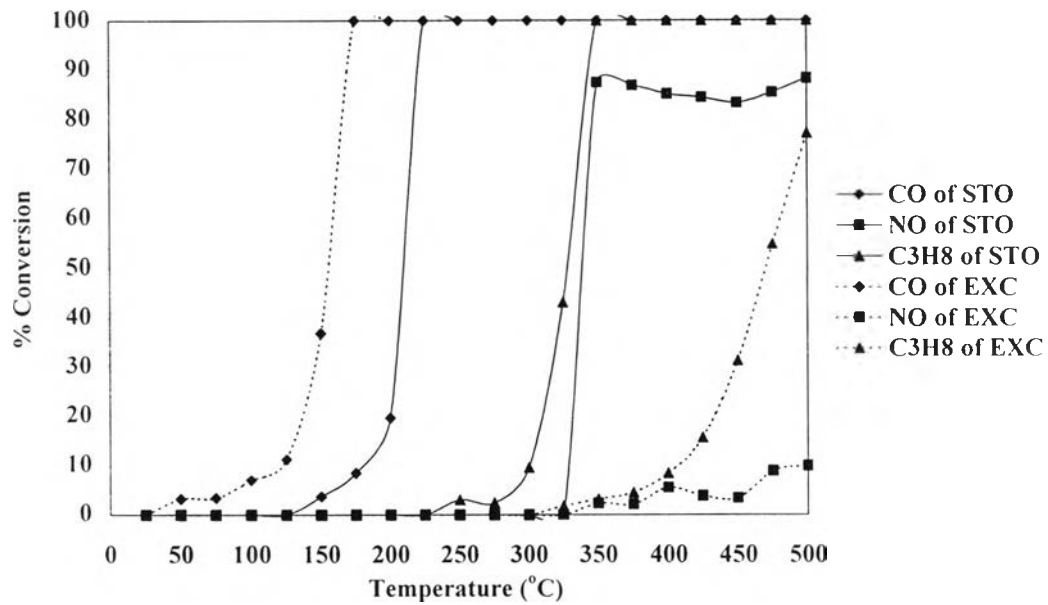
**Figure 6.20** Comparison of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> in metal form under lean-burn and stoichiometric conditions (STO = stoichiometric condition, EXC = lean-burn condition)



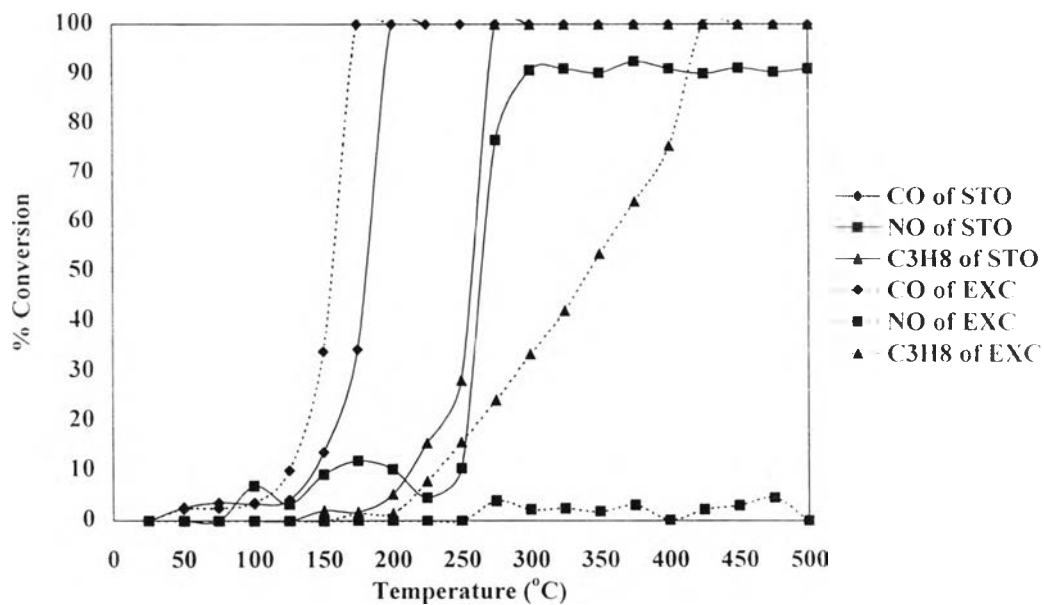
**Figure 6.21** Comparison of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> in SMSI form under lean-burn and stoichiometric conditions (STO = stoichiometric condition. EXC = lean-burn condition)



**Figure 6.22** Comparison of 0.3%Pt/TiO<sub>2</sub> in oxide form under lean-burn and stoichiometric conditions (STO = stoichiometric condition. EXC = lean-burn condition)



**Figure 6.23** Comparison of 0.3%Pt/TiO<sub>2</sub> in metal form under lean-burn and stoichiometric conditions (STO = stoichiometric condition, EXC = lean-burn condition)



**Figure 6.24** Comparison of 0.3%Pt/TiO<sub>2</sub> in SMSI form under lean-burn and stoichiometric conditions (STO = stoichiometric condition, EXC = lean-burn condition)

### **6.5.2 Comparison of catalytic activities measured from the oxide form, metal form and SMSI form catalysts**

Figure 6.25 demonstrates CO, C<sub>3</sub>H<sub>8</sub> and NO conversions of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> on oxide form, metal form and SMSI form catalysts. It is found that the metal form catalyst gives the same CO, C<sub>3</sub>H<sub>8</sub> and NO conversion as the SMSI form catalyst whereas the oxide form catalyst gives the lower values. Additionally, it is observed that the catalytic activity behavior under lean-burn condition is similar to that under stoichiometric condition.

Figure 6.26 illustrates CO, C<sub>3</sub>H<sub>8</sub> and NO conversions of 0.3%Pt/TiO<sub>2</sub> in oxide form, metal form and SMSI form catalysts. It is observed that CO conversions of the metal form and the SMSI form catalyst are the same but the oxide form catalyst gives the lowest CO conversion. The activity order for C<sub>3</sub>H<sub>8</sub> oxidation is found to be the SMSI form catalyst > the oxide form catalyst > the metal form. Moreover, the NO conversion of all catalyst is closed to the zero value.

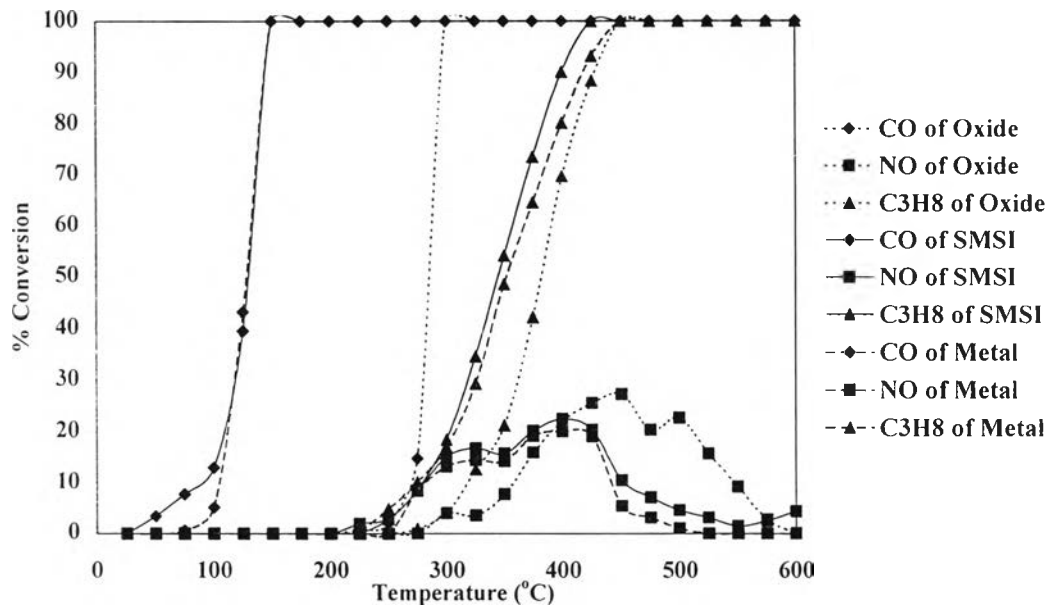


Figure 6.25 Comparison of CO, C<sub>3</sub>H<sub>8</sub> and NO conversions of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in oxide form, metal form and SMSI form, under lean burn condition

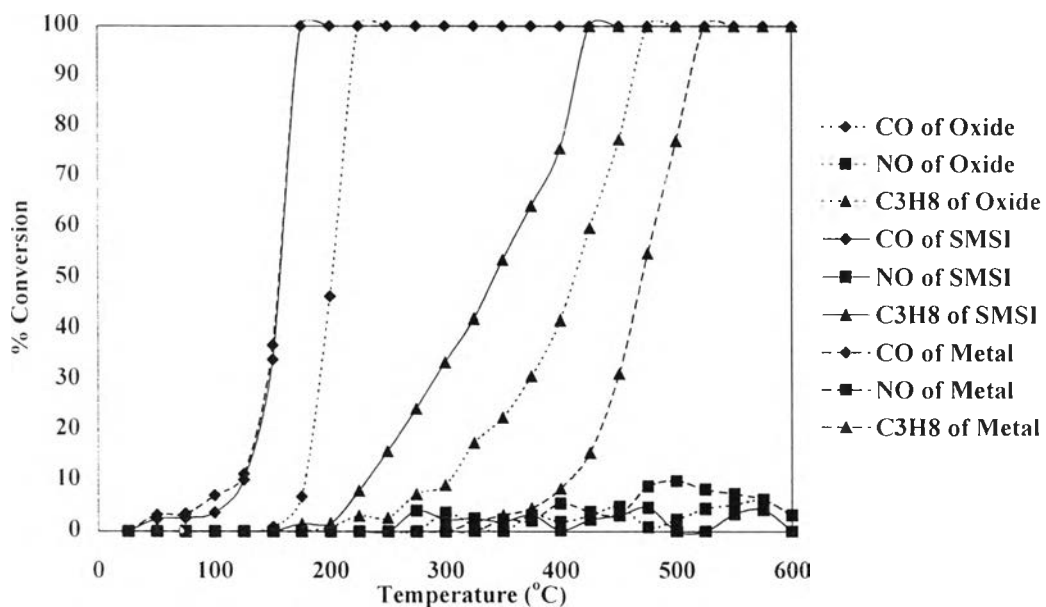
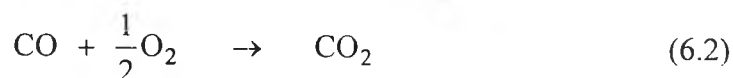
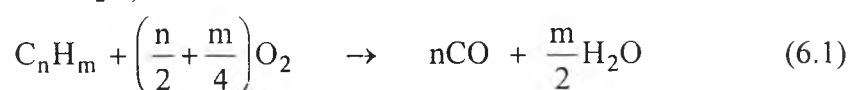


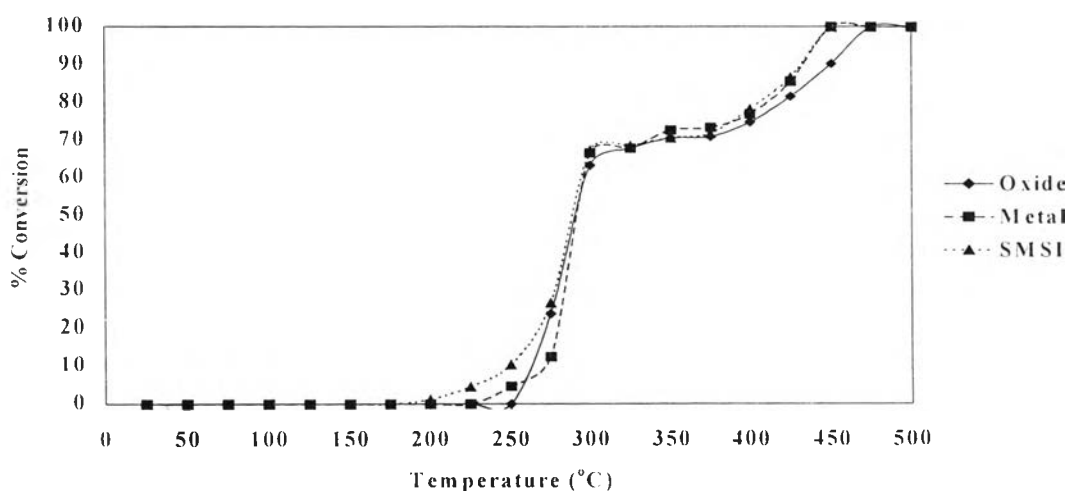
Figure 6.26 Comparison of CO, C<sub>3</sub>H<sub>8</sub> and NO conversions of 0.3%Pt/TiO<sub>2</sub> catalyst in oxide form, metal form and SMSI form, under lean burn condition

## 6.6 Discussion

Hautman *et al.*[59], reported that the hydrocarbons are rapidly consumed during combustion, forming CO, H<sub>2</sub> and H<sub>2</sub>O. The oxidation of CO to CO<sub>2</sub> proceeds somewhat more slowly. The difference in reaction rates can be taken into account using two-step models that are only slightly more complicated than the single-step model but can separate the relatively slow oxidation of CO to CO<sub>2</sub> from the more rapid oxidation of the hydrocarbon to CO and H<sub>2</sub>O, that is



From these two equations, it is believed that when the combustion is occurred, CO is presented. CO will react with NO and produce N<sub>2</sub> and CO<sub>2</sub>. Therefore, it must be demonstrated whether or not CO is occurred in the reaction. Conversion of C<sub>3</sub>H<sub>8</sub> combustion of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> in three forms tested under rich condition, which contains 2150 ppmC<sub>3</sub>H<sub>8</sub>, 8600 ppmO<sub>2</sub> and without CO and NO (S=0.8), are shown in Figure 6.27. It is observed that conversions of C<sub>3</sub>H<sub>8</sub> combustion of three forms are the same. Table 6.4 shows balanced C in this reaction.

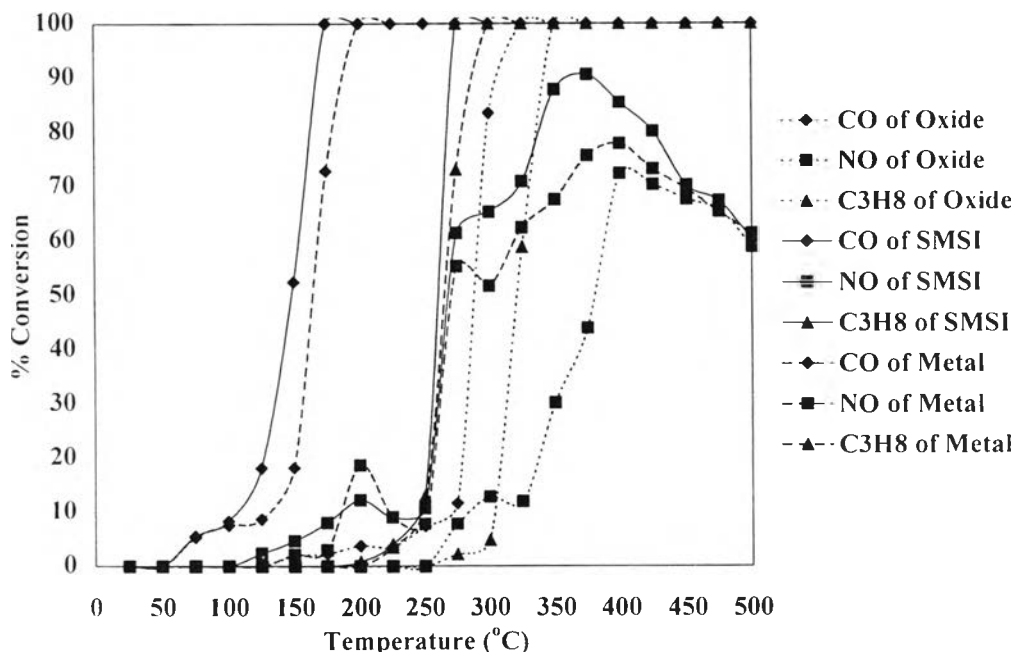


**Figure 6.27** Comparison of the catalyst activity for C<sub>3</sub>H<sub>8</sub> combustion reaction on three form catalysts. Feed composition: S = 0.8

**Table 6.4** Balanced C atom in C<sub>3</sub>H<sub>8</sub> combustion at S=0.8

Temp (°C)	Oxide form			Metal form			SMSI form		
	C loss in C <sub>3</sub> H <sub>8</sub> (ppm)	C in CO (ppm)	C in CO <sub>2</sub> (ppm)	C loss in C <sub>3</sub> H <sub>8</sub> (ppm)	C in CO (ppm)	C in CO <sub>2</sub> (ppm)	C loss in C <sub>3</sub> H <sub>8</sub> (ppm)	C in CO (ppm)	C in CO <sub>2</sub> (ppm)
200	0	0	0	0	0	23	0	0	63
225	0	0	0	0	0	93	243	0	229
250	0	0	73	360	0	322	612	0	746
275	1830	0	1518	972	0	1026	1887	0	1273
300	4881	0	4585	5192	0	4680	4905	0	4481
325	5226	0	4656	5295	0	4678	4992	0	4501
350	5436	0	4700	5664	0	4734	5154	0	4498
375	5463	0	4781	5718	0	4807	5232	0	4593
400	5754	0	4858	6000	629	4969	5715	757	4679
425	6282	776	4981	6666	1009	5101	6330	1157	4810
450	6942	1219	5088	7779	1606	5217	7302	1969	4825
475	7683	1554	5063	7779	2457	5232	7302	2634	4747
500	7683	2443	4965	7779	2759	5235	7302	2971	4693

Figure 6.28 shows conversions of CO, C<sub>3</sub>H<sub>8</sub> and NO of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> in three forms, under stoichiometric condition. It is observed that at the reaction temperature range between 250-300°C, NO conversion of the metal form and the SMSI form catalysts are rapidly increased with increasing temperature and there is no CO observed. NO conversion at the temperature above 400°C over the three form catalysts is nearly similar and there is a substantial amount of CO formed.



**Figure 6.28** Comparison of CO, C<sub>3</sub>H<sub>8</sub> and NO conversions of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in three forms, under stoichiometric condition (S=1)

From the experimental results, it is interestingly observed that NO conversion did not reach 100% at 100% CO and hydrocarbon conversion [3, 60]. This may possibly due to the conversion of NO to N-containing species.

As shown in Figure 6.28, NO conversions of the three-catalysts. i.e., oxide form, metal form and SMSI form catalyst, are affected by these following parameters:

#### 1. Effect of C<sub>3</sub>H<sub>8</sub> conversion

At the temperature range between 250-300°C, it is found that NO conversions of SMSI and metal forms are dramatically increased with C<sub>3</sub>H<sub>8</sub> conversion. Hydrocarbon combustion induces NO reduction at the condition that the light-off temperature is high enough to allow the NO activation but not too high to prevent from a too strong activity of O<sub>2</sub> for combustion and adsorption [58]. When C<sub>3</sub>H<sub>8</sub> reacts with O<sub>2</sub> on the catalyst surface, gas phase products are produced, consequently, the active sites of the catalyst will be available. As a result, NO in gas phase will adsorb on these sites and subsequently dissociate to N<sub>2</sub>.



## 2. Effect of catalyst form

In order to be assured that the NO reduction is affected only upon the catalyst form, the reaction temperature of 350°C at which the C<sub>3</sub>H<sub>8</sub> oxidation reaches 100% (see Figure 6.28), is considered. Figure 6.29 shows the stability of catalyst for NO conversion to N<sub>2</sub> at 350°C. The activity order for NO conversion is found to be;

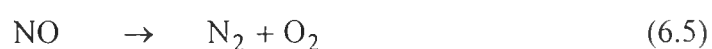
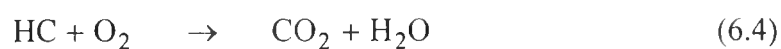
SMSI form > metal form > oxide form

In this experiment, the catalysts were heated to 500°C under exhaust gas condition before cooling down to 350°C and held for 150 minutes. It is shown that NO conversion to N<sub>2</sub> at 350°C and 500°C is not similar. It can increase and decrease of NO conversion to N<sub>2</sub> with the temperature changing. This can be explained that the O<sub>2</sub> coverage over the catalyst surface is reversible phenomena. Especially, it is observed that SMSI form gives the best all conversions at 350°C.

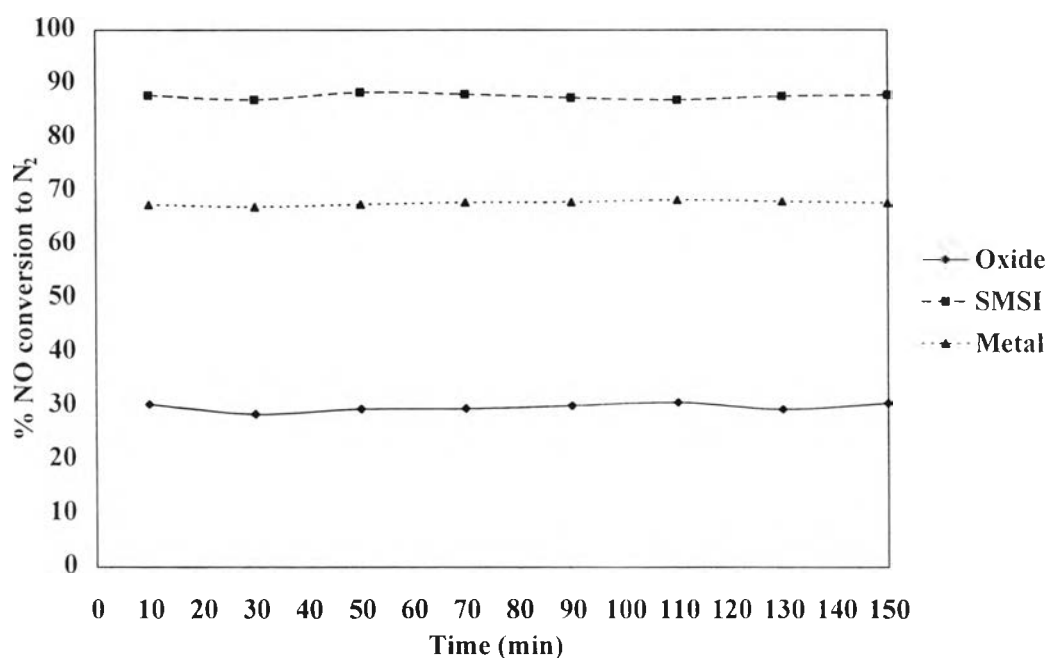
## 3. Effect of O<sub>2</sub> surface coverage

From Figure 6.28, NO conversions of three catalysts decrease after 400°C to the same conversion at 500°C. Figure 6.30 shows the stability of catalyst for NO conversion to N<sub>2</sub> at 500°C. It is found that NO conversions of three catalysts are approximately similar because the oxygen surface coverage decreases when increase temperature and the limited amount of oxygen is observed to affect the dissociation of NO, resulting in the NO conversion [61].

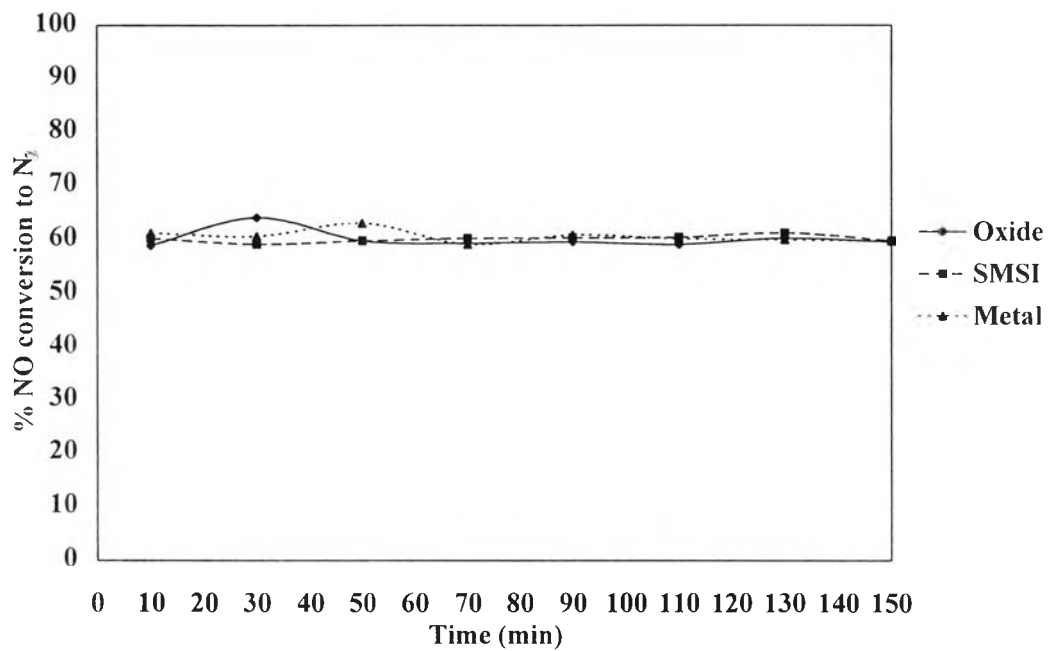
From the results, the mechanisms of the reaction between CO, NO and C<sub>3</sub>H<sub>8</sub> over Pt/Al<sub>2</sub>O<sub>3</sub> are;



Since at low temperature, CO would react well and hydrocarbon combustion would result in the availability of active site, therefore NO is adsorbed and then converted to N<sub>2</sub>.



**Figure 6.29** NO conversion to N<sub>2</sub> of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> in three form catalysts at 350°C under stoichiometric condition



**Figure 6.30** NO conversion to N<sub>2</sub> of 0.3%Pt/Al<sub>2</sub>O<sub>3</sub> in three form catalysts at 500°C under stoichiometric condition