

## CHAPTER V

### RESULTS AND DISCUSSION

This study is divided into four sections. The first two sections deal with the effect of various conditions on thermal pretreatment in the oxidation of CO and propane. The last two sections are aimed at the study of catalytic performance of the Pt on alumina support and on washcoat monolithic catalysts. The catalytic activity is compared using 'light-off temperature'; the temperature at which a 50% conversion is reached with respect to the gas being converted [6]. That is to say the lower the light-off temperature, the higher the catalytic activity. The catalyst, impregnated, dried and calcined in forced air at 500 °C for 4 hr will be called "Calcined catalyst" through out this thesis. Whereas the catalyst, impregnated, dried, and pretreated in simulated exhaust gas will be called "Pretreated catalyst".

The nomenclature in this chapter is listed below :

$S_1$  = stoichiometric number of gas composition for catalyst pretreatment

$S_2$  = stoichiometric number of gas composition for catalyst reaction

#### 5.1 Comparison between calcined and pretreated catalysts.

In this section, the study begins with decreasing calcination time of catalysts prepared from two different platinum precursor salts. Then, the study is aimed on the effect of various thermal pretreatment temperature

from 300 °C to 500 °C for carbon monoxide and propane oxidation in 2.5% excess oxygen ( $S_2= 2.0$ ) exhaust gas composition.

#### 5.1.1 Effect of decreasing time of calcination

Two different type of platinum precursor salts, Chloroplatinic acid [ $H_2PtCl_6$ ] and Tetrammine platinum dichloride(II) [ $Pt(NH_3)_4Cl_2$ ], were used to prepare 0.03 wt% Pt/ $Al_2O_3$  catalyst. All samples are listed in Table 5.1. The catalysts were calcined in air at 500 °C but had decreased the holding time from 240 min. to 20 min.

Table 5.1 Calcination conditions of catalysts prepared from two precursor salts: Pt content 0.03 wt%

Name of Catalyst	Precursor salts	Calcination Conditions
CAT. 1	$Pt(NH_3)_4Cl_2$	Calcined in air at 500°C 240 min.
CAT. 2	$Pt(NH_3)_4Cl_2$	Calcined in air at 500°C 20 min.
CAT. 3	$H_2PtCl_6$	Calcined in air at 500°C 240 min.
CAT. 4	$H_2PtCl_6$	Calcined in air at 500°C 20 min.

Figures 5.1 and 5.2 showed the effect of decreasing calcination time on propane ( $C_3H_8$ ) and CO conversions of the catalysts prepared from two precursor salts. The reaction was carried out in temperature range 150-700 °C. It was showed in Figure 5.1 that propane conversion of CAT.1 gradually increased from 150-300 °C. Then, it sharply increased from 300 °C to its 100% maximum conversion at 500 °C and still kept in this level at 500-700 °C. The similar trend was observed for the others sample at high temperature but the curves began to increase at 350 °C.

Figure 5.2 shows that CO conversion of CAT. 1 sharply increased from 150 °C to 100% maximum conversion at 200 °C without any decrease over high temperature. This situation was also observed for other samples but the curves began to increase at temperature higher than 200 °C. CAT.2 became active at 200 °C and reached its maximum conversion at 300 °C. The others became at 250-400 °C.

It was noted that there was a little difference between light-off temperatures of the C<sub>3</sub>H<sub>8</sub> conversion for the samples prepared from H<sub>2</sub>PtCl<sub>6</sub> (CAT.3 and CAT.4). While the catalysts prepared from Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> (CAT.1 and CAT.2) showed a larger difference in light-off temperature. Note that catalyst calcined for 240 min. had lower light-off temperature than calcination for 20 min. However, there were differences in catalytic activity between samples prepared from two precursor salts. That was, CAT.1 had the lowest light-off temperatures for both CO and C<sub>3</sub>H<sub>8</sub> conversion; and CAT.3, with the calcination that decreased to 20 min., still had a lower light-off temperature than both CAT.2 and CAT.4. The light-off temperatures of each catalyst were summarized in Table 5.2 below.

Table 5.2 The light-off temperature of catalysts with decreasing calcination time.

Catalysts Name	Light-off Temperature(°C)	
	of C <sub>3</sub> H <sub>8</sub> Conv.	of CO Conv.
CAT.1 (240 min)	360	175
CAT.2 ( 20 min)	400	255
CAT.3 (240 min)	380	325
CAT.4 ( 20 min)	390	350

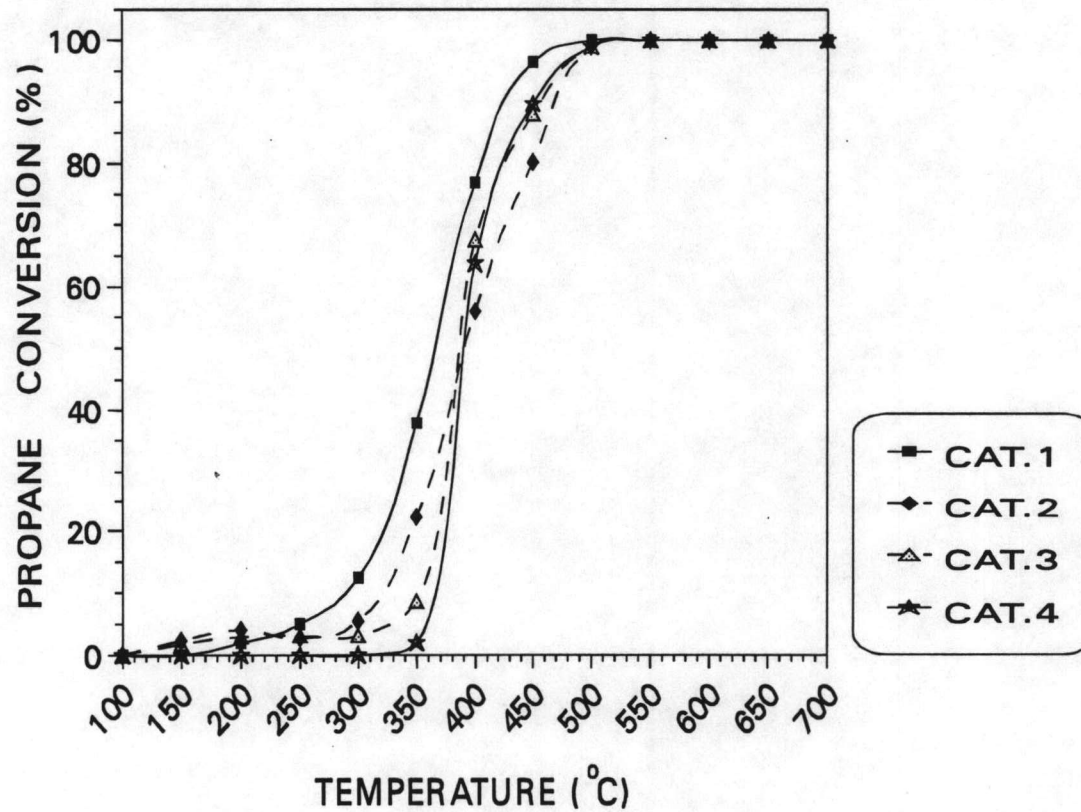


Figure 5.1 Effect of calcination time and precursor salts on Pt/Al<sub>2</sub>O<sub>3</sub> for Propane Conversion, GHSV = 15,000 h<sup>-1</sup> Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)

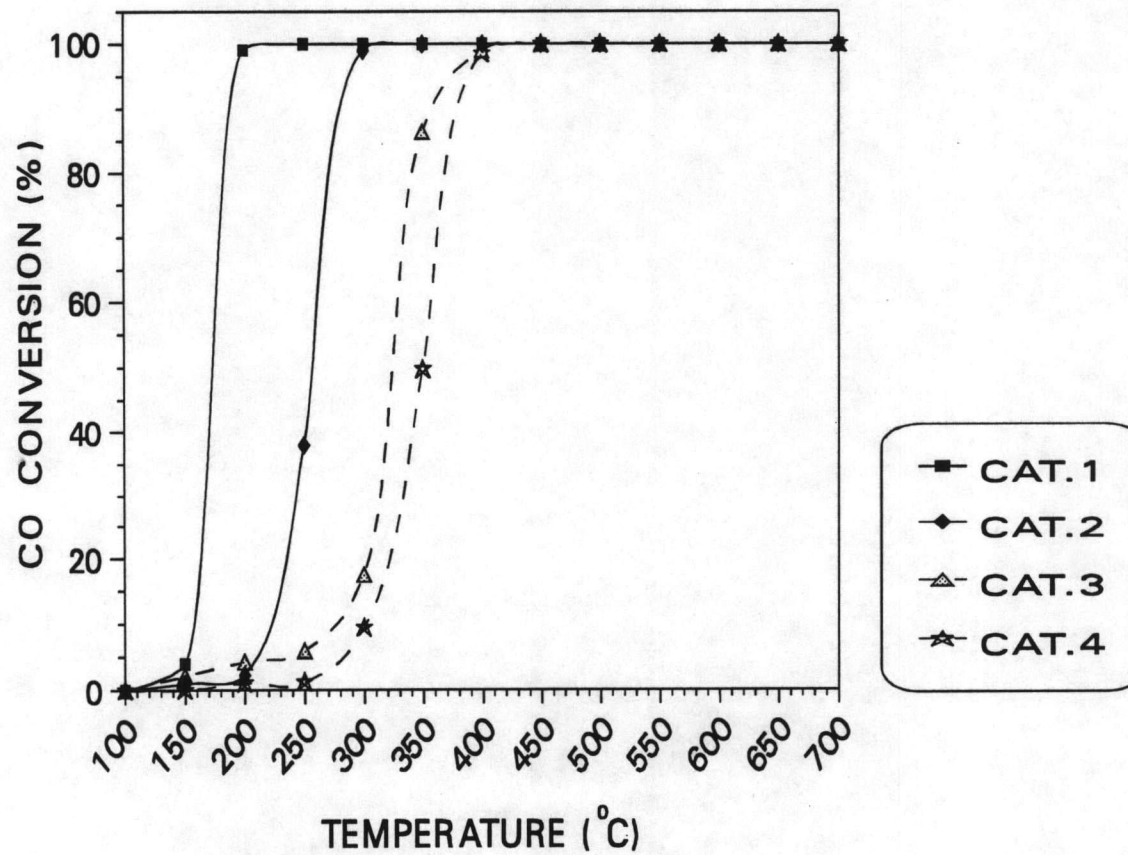


Figure 5.2 Effect of calcination time and precursor salts on Pt/Al<sub>2</sub>O<sub>3</sub> for CO Conversion, GHSV = 15,000 h<sup>-1</sup>  
 Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)



### 5.1.2 Effect of temperature on thermal pretreatment

In this part, the catalysts were pretreated in the temperature that range of 300-500 °C in rich condition ( $S_1=0.8$ ) for a constant time of 2 hr. as shown in Table 5.3 below.

Table 5.3 Catalysts pretreated in the various pretreatment temperature.

Name of catalyst	Precursor salts	Pretreatment Conditions
CAT. 1 (ref. cat.)	$Pt(NH_3)_4Cl_2$	Calcined in air at 500°C 4 hr.
CAT. 3 (ref. cat.)	$H_2PtCl_6$	Calcined in air at 500°C 4 hr.
CAT.5	$Pt(NH_3)_4Cl_2$	300°C
CAT.6	$H_2PtCl_6$	300°C
CAT.7	$Pt(NH_3)_4Cl_2$	400°C
CAT.8	$H_2PtCl_6$	400°C
CAT.9	$Pt(NH_3)_4Cl_2$	500°C
CAT.10	$H_2PtCl_6$	500°C

Figures 5.3 and 5.4 show the effect of pretreatment temperature between 300-500 °C on propane and CO conversion of catalyst prepared from two precursor salts. Figure 5.3 shows that all curves played a similar trend that the conversion gradually increased at 150-200 °C. After that, the conversion was sharply increased at 250-500 °C. After the maximum conversion was reached, the conversion did not show any decrease at high temperature. Catalysts prepared from both precursor salts, showed a significant effect of pretreatment temperature on their light-off temperature

that the higher pretreatment temperature, the lower light-off temperature. For instance, CAT.9 and CAT.10 which prepared from  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$  and  $\text{H}_2\text{PtCl}_6$  precursor respectively. Their conversions started to increase at 200 °C and reached the maximum conversion at 450 °C. There were a little differences in their conversions while increased temperature.

Figure 5.4 shows the CO conversions of all prepared catalysts. The CO conversions of all samples sharply increased at 150 °C and reached 100% conversion at 200 °C, except two catalysts (CAT.3 and CAT.5) which prepared from  $\text{H}_2\text{PtCl}_6$  precursor. CO conversion of catalyst pretreated at 300 °C, CAT.5, increased at 200 °C and reached 100% conversion at 250 °C. While conversion of a calcined catalyst, CAT.3, was increased at 250 °C and reached the maximum conversion at 450 °C.

It was observed that the catalytic activity of the catalysts pretreated in temperature that range between 300-500°C (CAT.5-CAT.10) for  $\text{C}_3\text{H}_8$  conversion was higher than that of calcined catalysts (CAT.1 and CAT.3). Moreover, the catalytic activity of catalysts pretreated at 400-500°C did not seem to depend on the type of platinum precursor. Whereas the light-off temperature of the catalysts pretreated at 300 °C differ significantly in both  $\text{C}_3\text{H}_8$  and CO conversion as illustrated in Fig. 5.3 and 5.4 respectively. It could be suggested that precursor salts used have effect on the pretreatment at 300 °C.

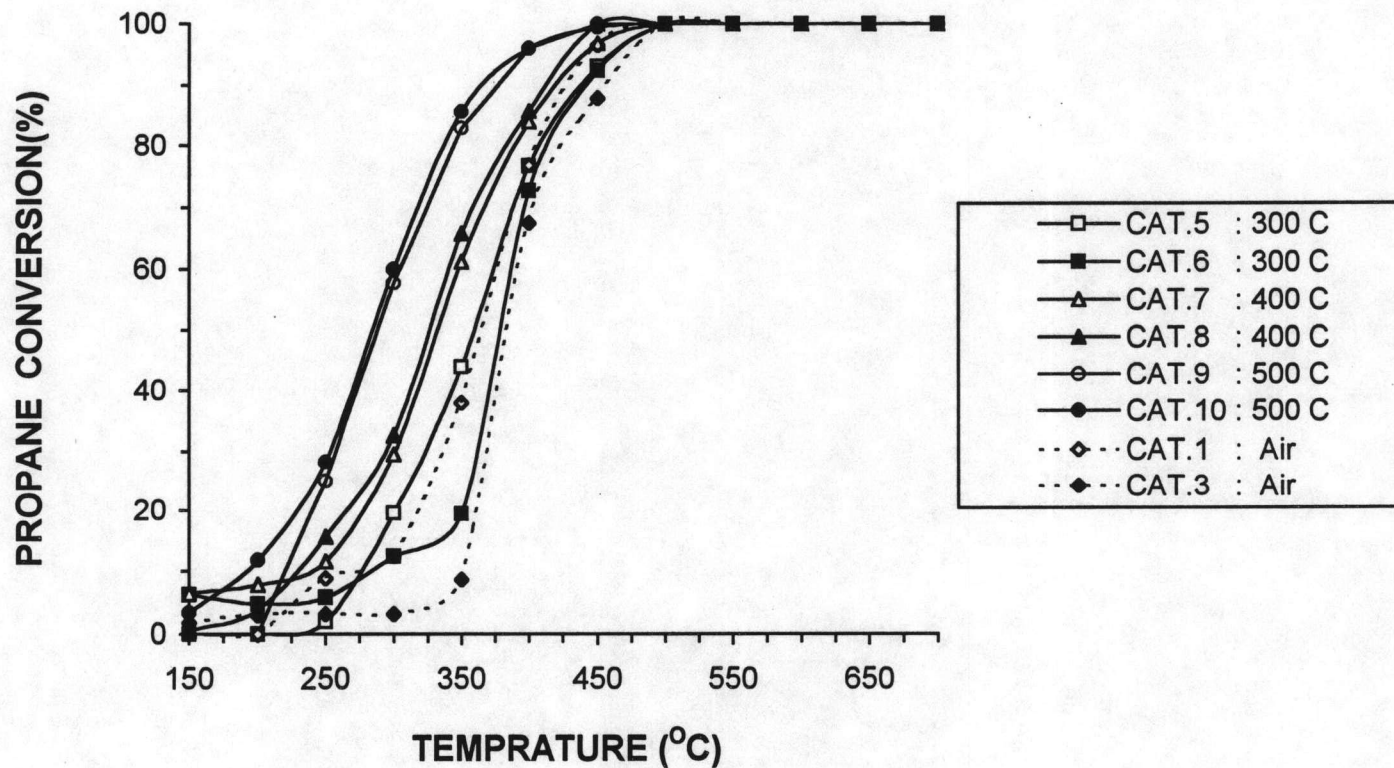


Figure 5.3 Effect of pretreatment temperature on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion by Pt/Al<sub>2</sub>O<sub>3</sub>, GHSV = 15,000 h<sup>-1</sup> Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)



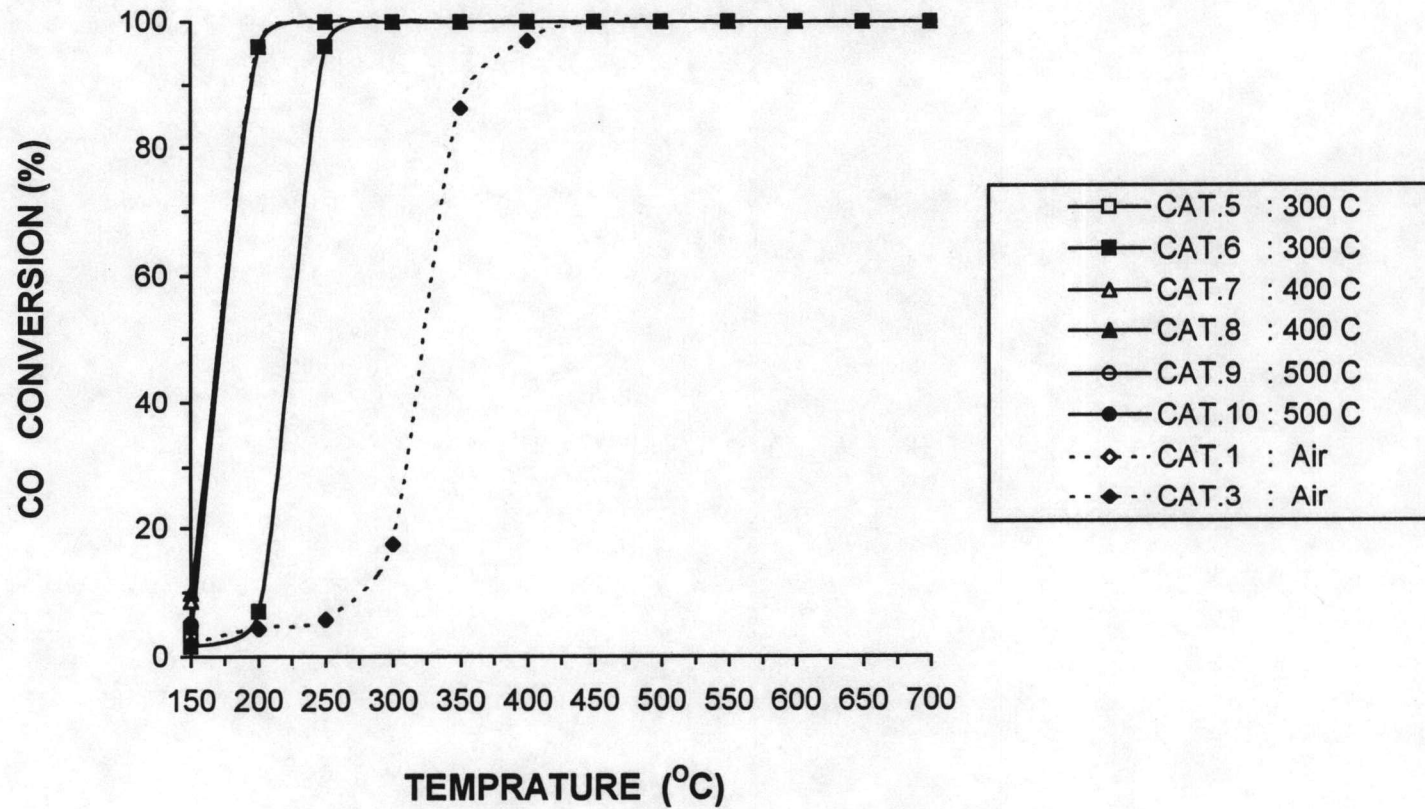


Figure 5.4 Effect of pretreatment temperature on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup>  
Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)

The explanation of the lost of activity may be explained by two reasons. The first reason, for the catalyst prepared using chloride containing precursor salts, is the effects of chloride proposed by Simone et al. [37], by (i) blocking metal oxide sites, thereby decreased the accessibility of the reactant gas to the catalytic site and/or (ii) chemical interaction of chloride with the catalytically active metal oxide species, resulting in metal oxide chloride complexes which are less active. These effects were detrimental under oxidizing conditions. Whereas, the results observed from catalyst prepared at 400 °C and 500 °C (CAT.8 and CAT.10) show an increase in the catalytic activity. The removal of chloride from the catalyst surface by water formed during the total oxidation of hydrocarbon would be responsible for this promoting effect, Marecot et al. [1]. The second reason, for the catalyst prepared using ammonium chloride containing salts, is from the beneficial effect of ammonium chloride which is relatively easily driven off by activating catalyst at 280 °C [38].

To prove these reasons, two catalysts were prepared from two different precursor salts. The first, CAT.11 is prepared using non-chlorinated precursor salt, Dinitro diammine platinum  $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ . The second, CAT. 12 is prepared using a platinum ammonium complex, complexing  $\text{H}_2\text{PtCl}_6$  with concentrated  $\text{NH}_4\text{OH}$ , which prepared by adding ammonium hydroxide into  $\text{H}_2\text{PtCl}_6$  solution in sufficient amount to form a platinum ammonia complex. The formation of a complex can be noted from the color of the solution which changes from an orange to a yellow. Where using an excess amount of ammonia has been found to be beneficial [38]. All samples were pretreated at 300 °C at  $S_1=0.8$  for 2 hr.

Table 5.3a Precursor salts used for prepare catalysts.

Name of Catalyst	Precursor salts
CAT. 5	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$
CAT. 6	$\text{H}_2\text{PtCl}_6$
CAT. 11	$\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$
CAT. 12	$\text{H}_2\text{PtCl}_6 + \text{NH}_4\text{OH}$

Figures 5.4a and 5.4b show the effect of catalysts prepared from different precursor salts. Figure 5.4a show that all propane conversion gradually increased between 150-300 °C. Then, they sharply increased at 300 and reached 100% maximum conversion at 500 °C without any decrease at high temperature.

Figure 5.4b shows CO conversion of the prepared catalysts. All curves sharply increased between 150-200 °C but the catalyst prepared from  $\text{H}_2\text{PtCl}_6$  (CAT.6) was excepted. Its conversion began to increase at 200 °C and reached 100% conversion at 250 °C.

The results of CO and propane conversion is showed in Figures 5.4a and 5.4b. The figures clearly show that the activity of platinum ammonia chloride catalyst (CAT. 12) is higher than that of the non-complexing chlorinated catalyst (CAT. 6). This results show the promoting effect of ammonium complex. Furthermore, CAT.11., prepared by using non-chlorinated ammonia precursor salt, did not have any improvement in the catalytic activity of propane conversion. That is to say, the catalyst prepared

by using precursor salt which has both ammonia and chloride shows a higher activity than those prepared from ammonia or chloride precursor salt only.

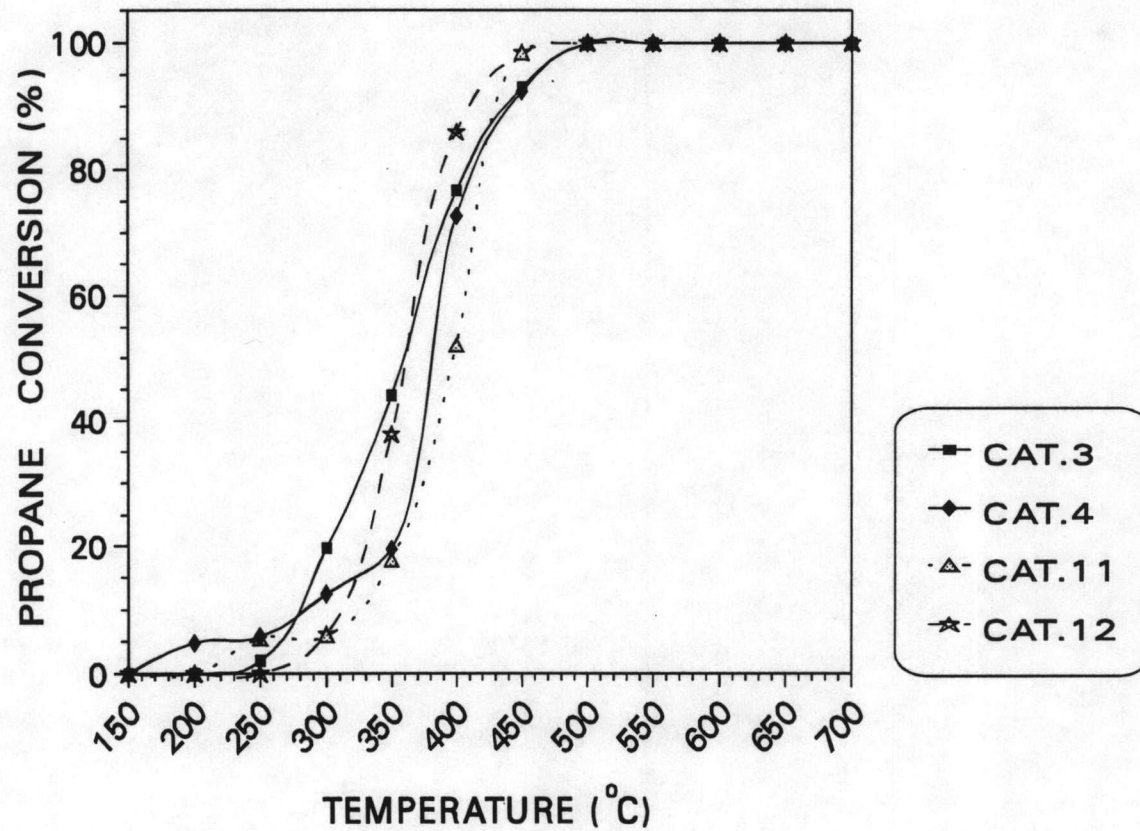


Figure 5.4a Effect of precursor salts on pretreated Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup>, S<sub>1</sub> = 0.8 Feed composition at excess O<sub>2</sub> (S<sub>2</sub> = 2.0)

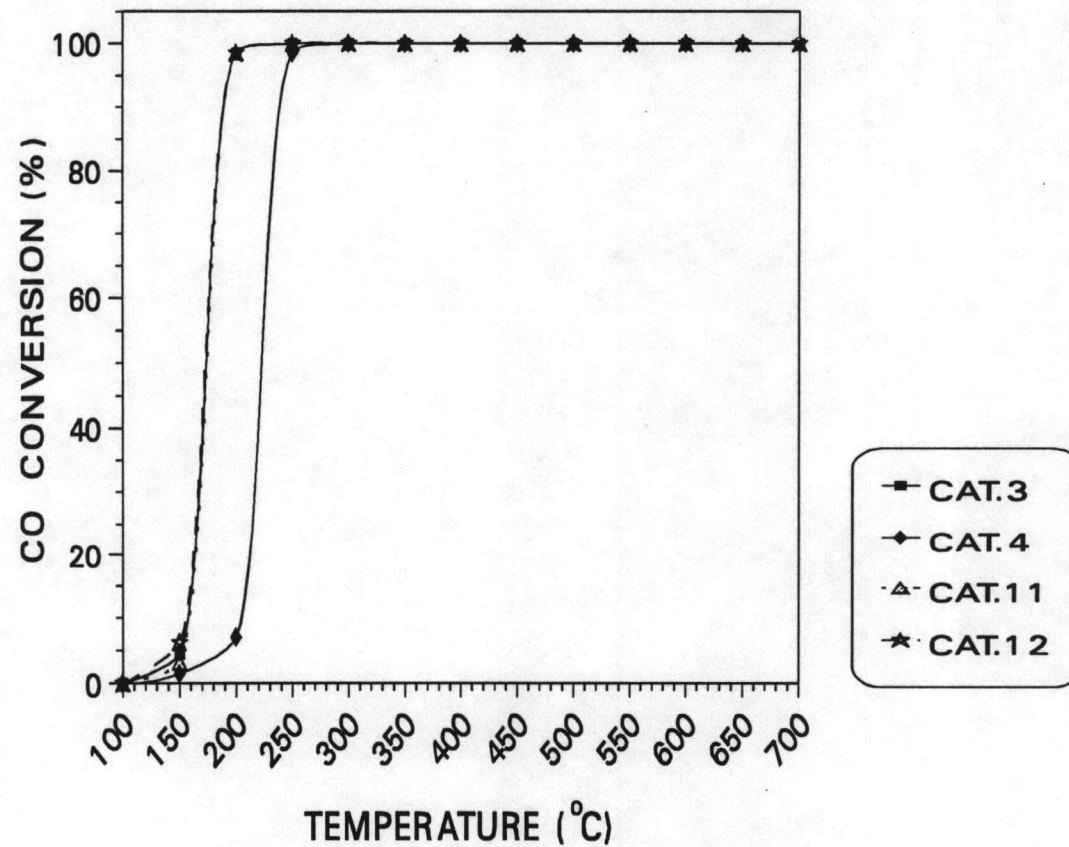


Figure 5.4b Effect of precursor salts on pretreated Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup>, S<sub>1</sub> = 0.8  
Feed composition at excess O<sub>2</sub> (S<sub>2</sub> = 2.0)

## 5.2 Effect of Various Conditions on Thermal Pretreatment

In the previous section, it was found that Pt/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> showed the best activity for both CO and C<sub>3</sub>H<sub>8</sub> conversion among the catalysts pretreated at 300-500°C. As a result, Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> was chosen to be the only main precursor salt use for the remaining study.

In this section, the effect of O<sub>2</sub> content in gas mixtures for pretreatment catalysts will be investigated first. Then, the effect of pretreatment temperature was studied. Finally, the samples pretreated in various holding time for pretreatment will be look upon.

### 5.2.1 Effect of O<sub>2</sub> content on thermal pretreatment

The samples were pretreated in different exhaust gas composition by varying O<sub>2</sub> content in gas feed stream from S<sub>1</sub>=0.8 (1.0 vol.%O<sub>2</sub>) to S<sub>1</sub>=2.0 (2.5vol.%O<sub>2</sub>) in temperature ranging between 300-500 °C. The sample pretreatment conditions are listed in Table 5.4.

Table 5.4 Catalyst pretreated in various O<sub>2</sub> content and temperature.

Catalyst name	Pretreatment condition
CAT.1	calcined in air at 500 °C
CAT.13	S1=0.6 (0.5 vol.%O <sub>2</sub> ), 300 °C
CAT.5	S1=0.8 (1.0 vol.%O <sub>2</sub> ), 300 °C
CAT.14	S1=1.0 (1.2 vol.%O <sub>2</sub> ), 300 °C
CAT.15	S1=2.0 (2.5 vol.%O <sub>2</sub> ), 300 °C
CAT.16	S1=3.5 (3.0 vol.%O <sub>2</sub> ), 300 °C
CAT.7	S1=0.8 (1.0 vol.%O <sub>2</sub> ), 400 °C
CAT.17	S1=1.0 (1.2 vol.%O <sub>2</sub> ), 400 °C
CAT.18	S1=2.0 (2.5 vol.%O <sub>2</sub> ), 400 °C
CAT.9	S1=0.8 (1.0 vol.%O <sub>2</sub> ), 500 °C
CAT.19	S1=1.0 (1.2 vol.%O <sub>2</sub> ), 500 °C
CAT.20	S1=2.0 (2.5 vol.%O <sub>2</sub> ), 500 °C

Figures 5.5, 5.7, and 5.9 show propane conversion of pretreated catalysts in rich, stoichiometric, and lean condition at 300-500 °C. Their propane conversions gradually increased between 150-250 °C. All curves began raising up at 250 °C and reached 100% maximum conversion at 450-500 °C, without any decrease at temperature higher than 500 °C. The order of curve raising was the catalyst prepared under rich, stoichiometric, and lean condition respectively.



Figures 5.6, 5.8, and 5.10 show that CO conversion sharply increased between 150-200 °C. There was no any differences in light-off temperature for all catalysts.

The thermal pretreatment study for propane conversion indicated that catalyst pretreated in rich condition (CAT.5, 7 and 9) showed a higher activity than catalyst pretreated in stoichiometric (CAT.14, 17 and 19) and lean (CAT. 15, 18 and 20) conditions for all considered temperature at 300-500 °C as shown in Figures. 5.5, 5.7, and 5.9, respectively. Besides, higher temperature for pretreatment seem to be connected with the higher activity of catalyst which can be observed from decreasing in light-off temperature when the pretreatment temperature was increased.

For the iso-thermal pretreatment at 300 °C, the samples pretreated in rich condition (CAT.5) showed the minimum activity but still better than catalyst calcined in air (CAT.1) which can be noted from the lower light-off temperature for propane conversion shown in Table 5.5.

Table 5.5 The light-off temperature of various O<sub>2</sub> content in pretreatment.

Catalysts Name	Light-off Temperature(°C)	
	For C <sub>3</sub> H <sub>8</sub> Conv.	For CO Conv.
CAT.1	360	175
CAT.17	355	175
CAT.9	355	175
CAT.18	375	175
CAT.19	380	175
CAT.20	400	175
CAT.7	350	175
CAT.15	355	175
CAT.16	370	175
CAT.5	280	175
CAT.13	320	175
CAT.14	320	175

Figures. 5.6, 5.8 and 5.10 show that the light-off temperature of CO conversion are in similar region for all samples. Therefore, it can be concluded that the catalytic activity for CO conversion did not depend on temperature and oxygen content in pretreatment exhaust gas.

To assure the dependence of activity of the catalyst by pretreatment on the quantity of O<sub>2</sub> mixed up in simulated exhaust gas, the catalysts were prepared in various O<sub>2</sub> content in gas mixtures. These catalysts are already listed in Table 5.5. From the experimental results, the catalyst which was pretreated in rich condition (CAT.5 and 13), showed higher activity, when

testing in  $C_3H_8$  conversion (Figure 5.9), than the catalysts pretreated in stoichiometric (CAT.14) and in lean condition (CAT.15 and 19). Moreover, only the catalysts pretreated in rich region played more activity than the catalyst calcined in air. The activity of the catalysts pretreated at a constant temperature (300 °C) can be classified as follows:

$$\text{CAT.13~CAT.5} > \text{CAT.1} > \text{CAT.14~CAT.15} > \text{CAT.16}$$

Similar to previous results, there were no significant change in light-off temperature of CO conversion (Figure 5.6).

From the above results, it could be concluded that the catalyst activity for propane conversion depends on temperature and oxygen content in gas mixture. On the other hand, CO conversion did not depend on both temperature nor oxygen content.

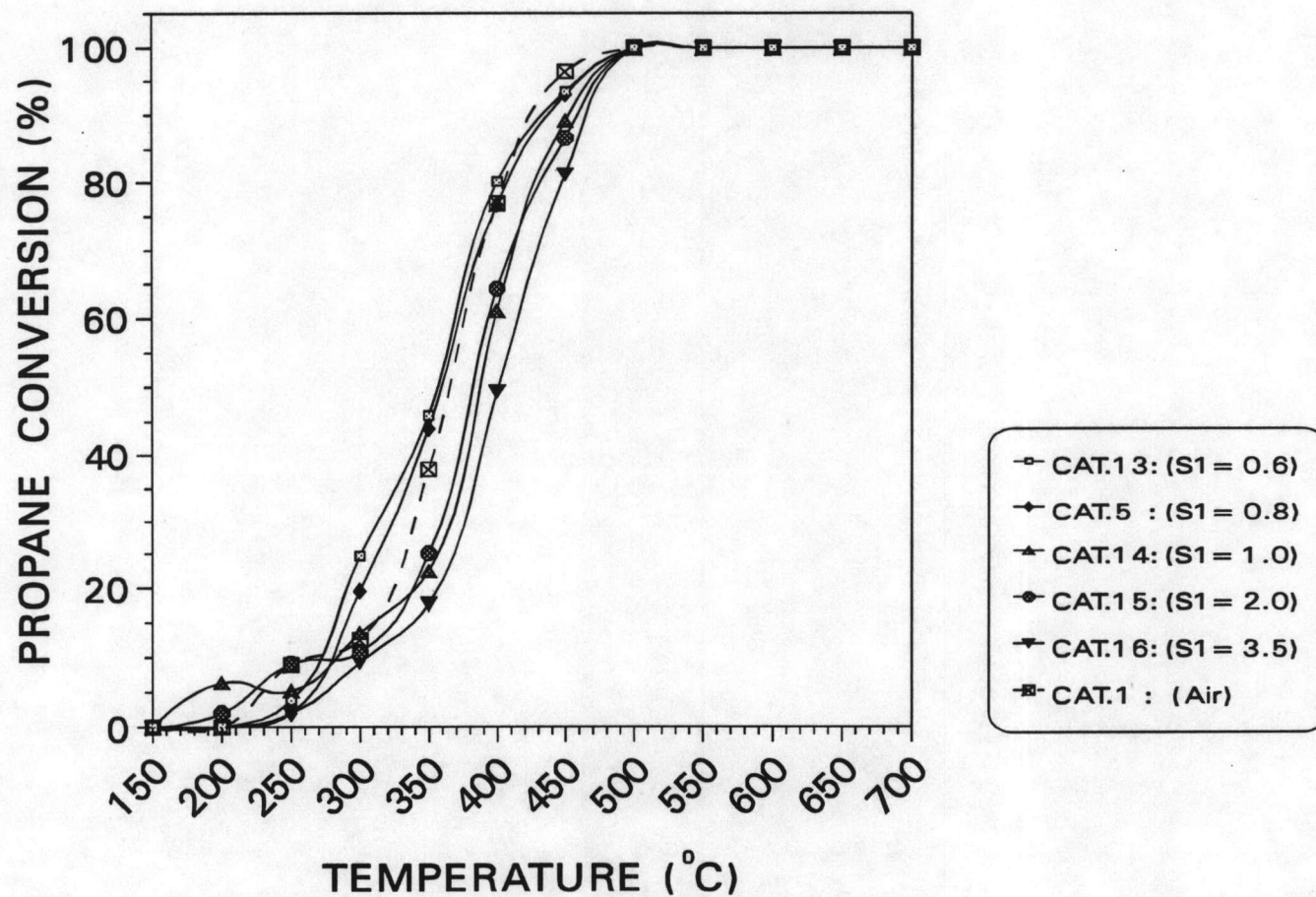


Figure 5.5 Effect of O<sub>2</sub> content for thermal pretreatment at 300 °C on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup>  
Feed composition at excess O<sub>2</sub> (S<sub>2</sub> = 2.0)

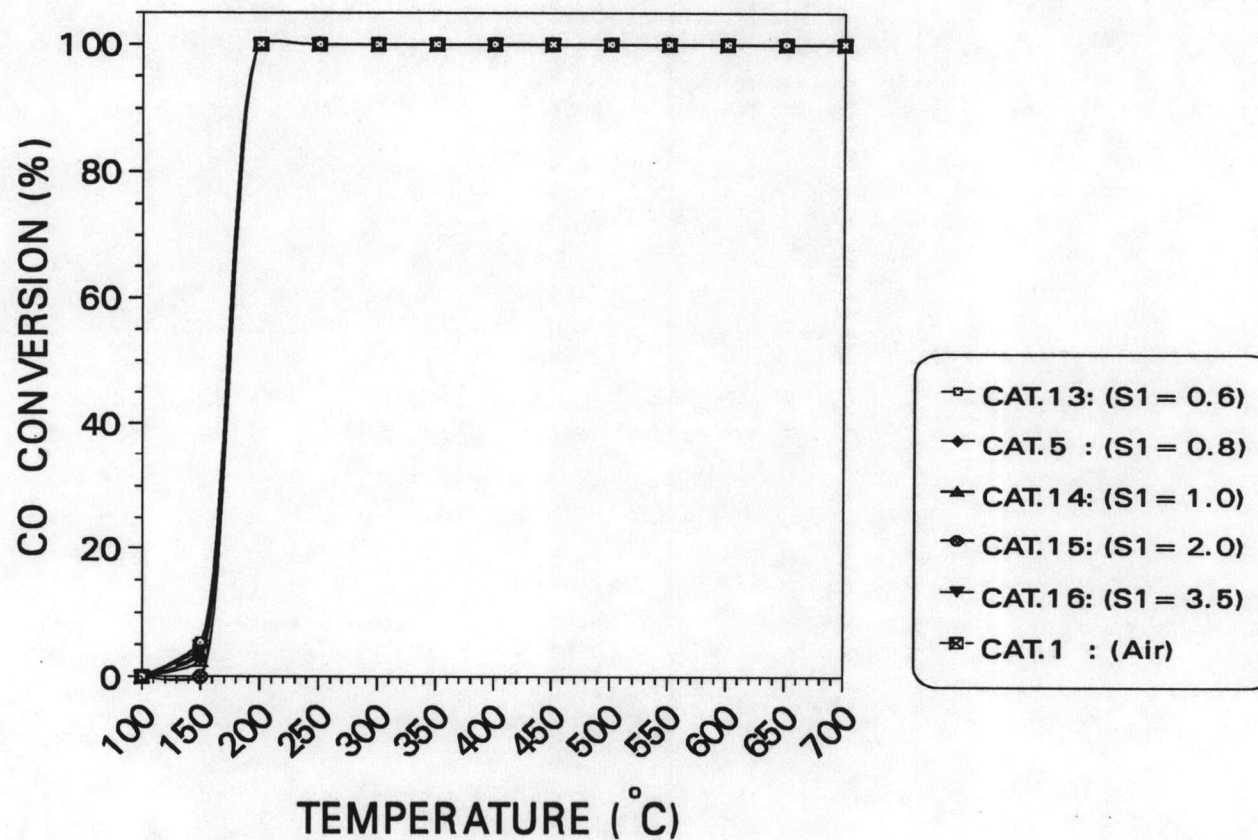


Figure 5.6 Effect of O<sub>2</sub> content for thermal pretreatment at 300 °C on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup>  
Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)

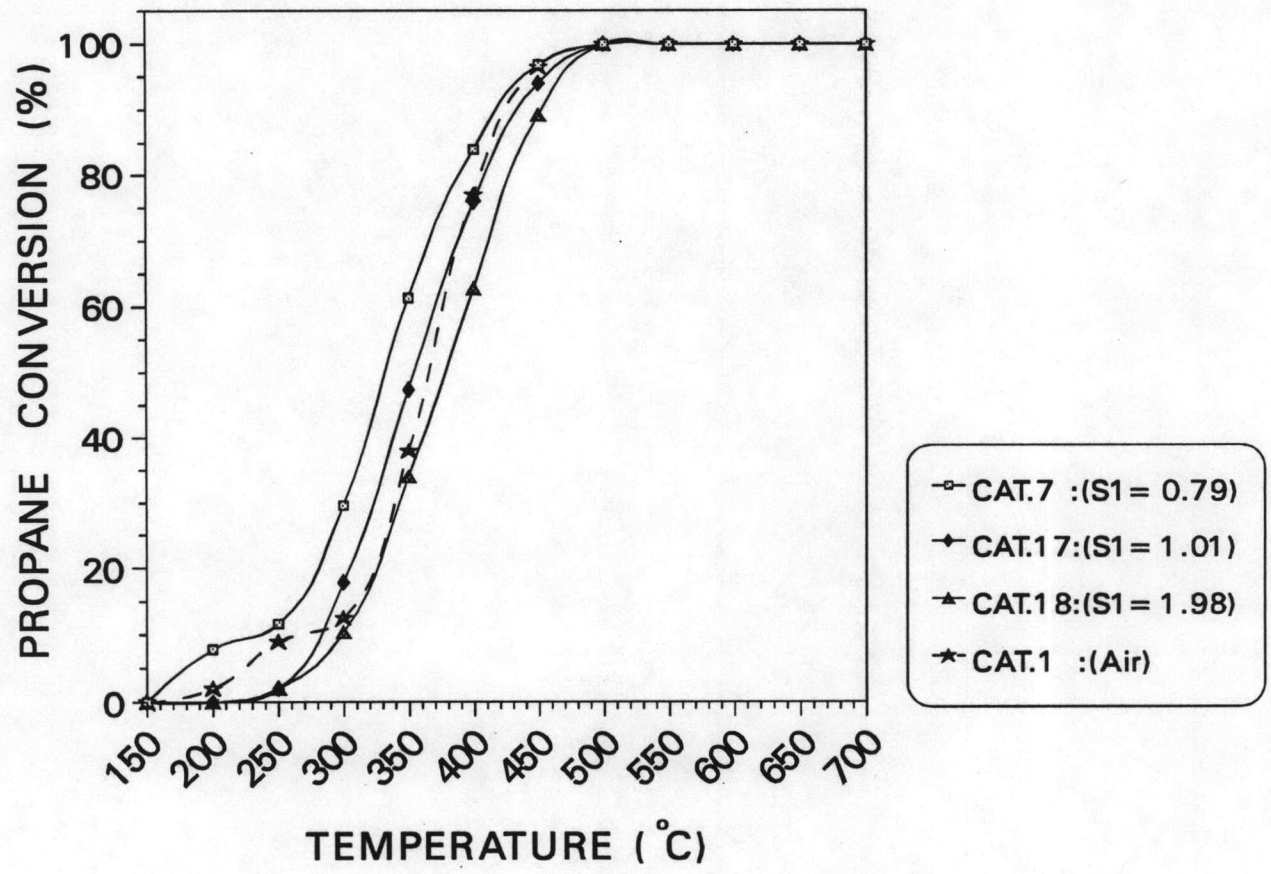


Figure 5.7 Effect of O<sub>2</sub> content for thermal pretreatment at 400 °C on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup> Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)

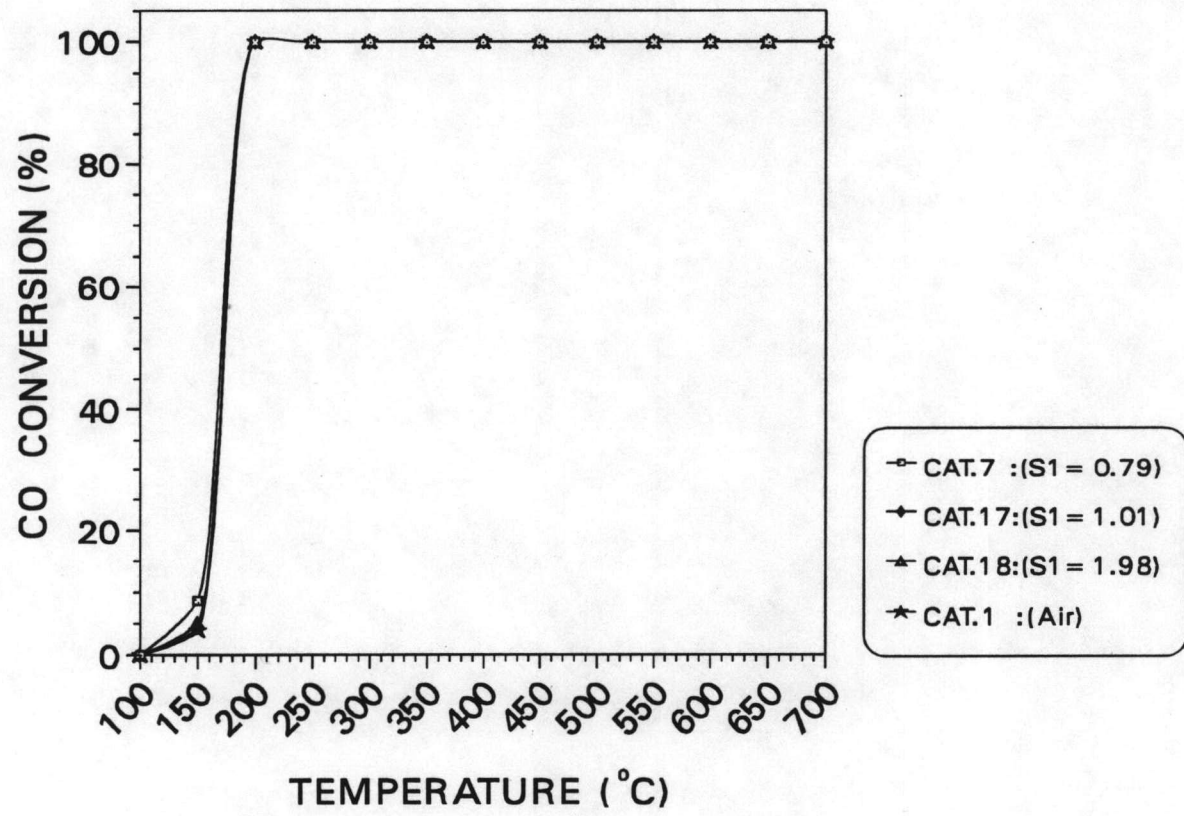


Figure 5.8 Effect of O<sub>2</sub> content for thermal pretreatment at 400 °C on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup> Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)

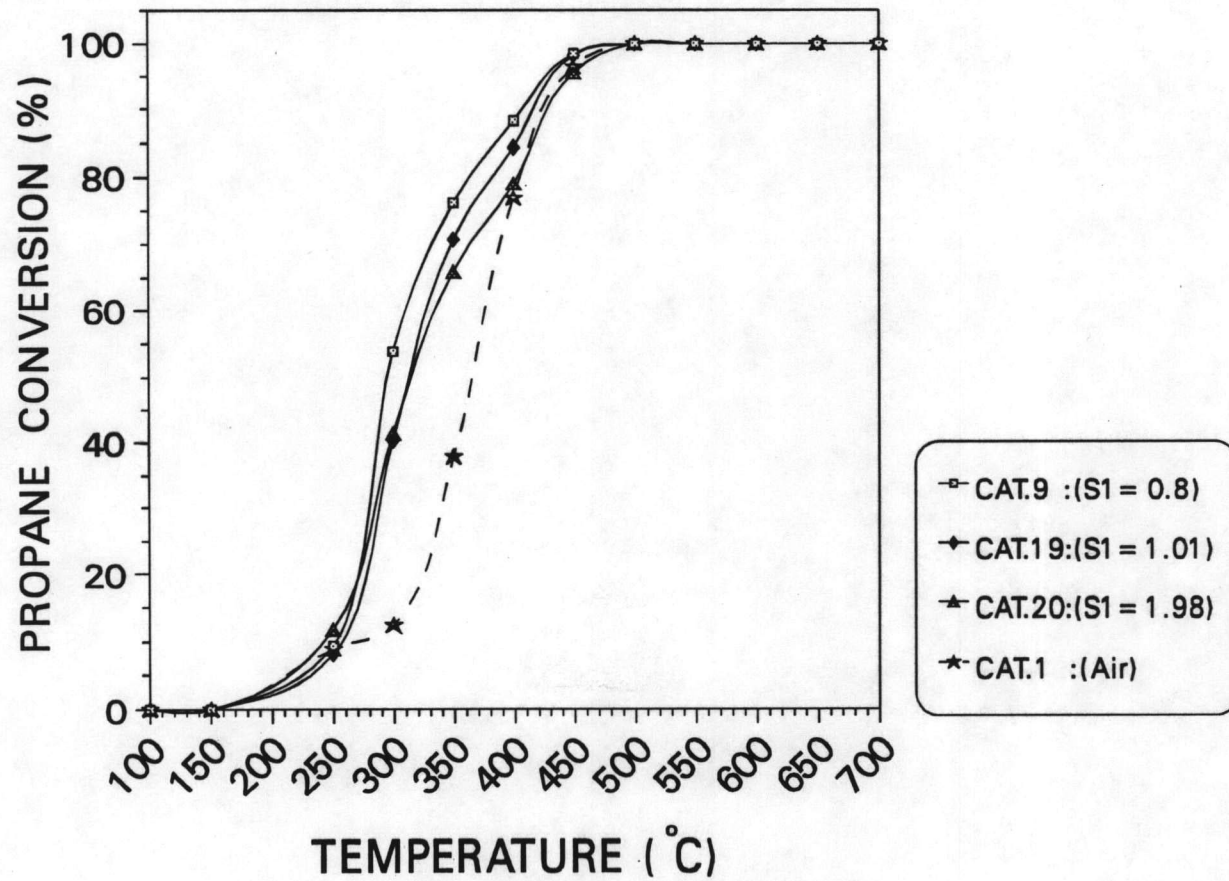


Figure 5.9 Effect of O<sub>2</sub> content for thermal pretreatment at 500 °C on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup> Feed composition at excess O<sub>2</sub> (S<sub>2</sub>= 2.0)





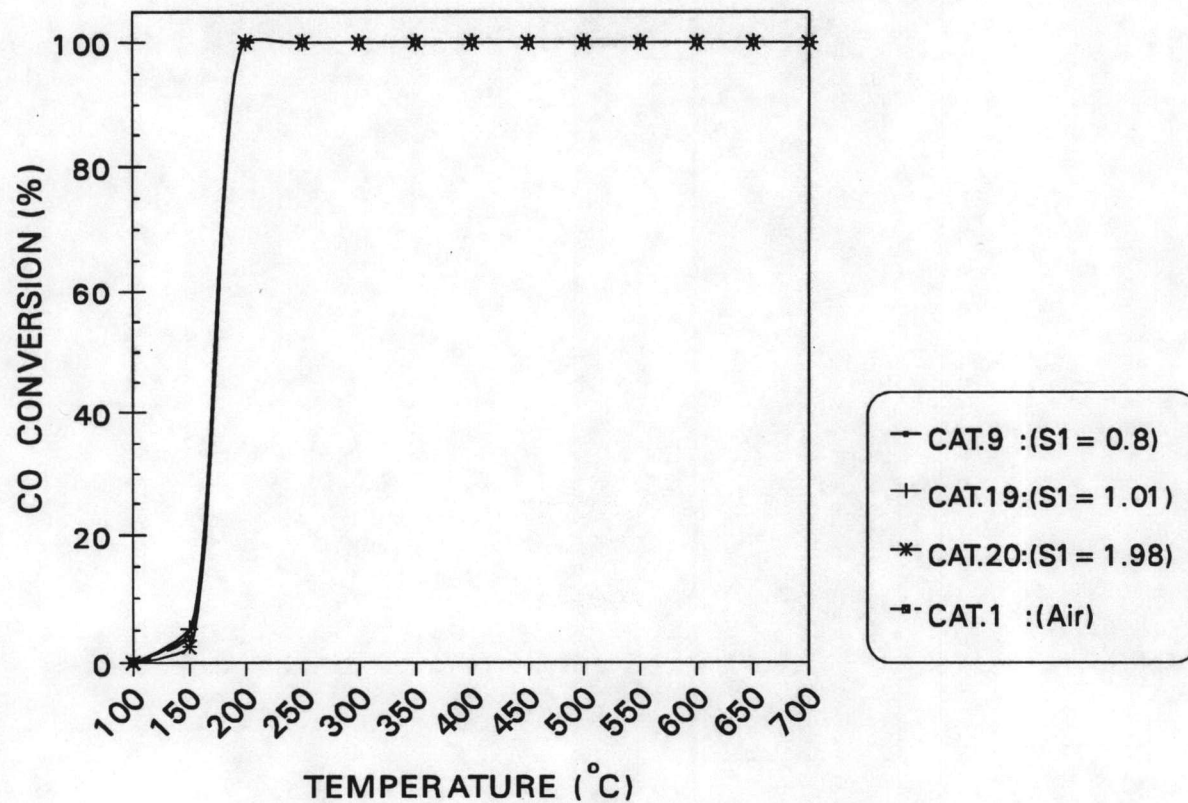


Figure 5.10 Effect of  $O_2$  content for thermal pretreatment at  $500\text{ }^\circ\text{C}$  on  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts for CO Conversion,  $\text{GHSV} = 15,000\text{ h}^{-1}$   
 Feed composition at excess  $O_2$  ( $S_2 = 2.0$ )

### 5.2.2 Effect of temperature on thermal pretreatment

All catalysts prepared in this section are listed in Table. 5.6 below:

Table 5.6 Catalysts pretreated in various pretreatment temperature.

Name of Catalyst	Pretreatment Conditions
CAT. 1	Calcined in air at 500 °C 4 hr.
CAT. 1a	Reduced CAT.1 at 500 °C 2 hr
CAT. 21	$S_1=0.8$ , 200 °C
CAT. 5	$S_1=0.8$ , 300 °C
CAT. 7	$S_1=0.8$ , 400 °C
CAT. 9	$S_1=0.8$ , 500 °C
CAT. 22	$S_1=0.8$ , 600 °C
CAT. 23	$S_1=0.8$ , 700 °C

Figure 5.11 shows the effect of pretreatment temperature between 200-700 °C on propane conversion. The conversion curves sharply increased with temperature range between 200-500 °C. For example, propane conversion of the catalyst pretreated at 700 °C (CAT.23) slightly increased at 100-200 °C and sharply increased at 200-400 °C until it reached its maximum conversion at high temperature, the propane conversion was stable at 100% conversion without any decrease at 500-700 °C. The light-off temperature slightly increased when pretreatment temperature was decreased.

Thermal pretreatment of the samples at various temperatures showed that the pretreatment at a low temperature of 200 °C (CAT.21) causes a

higher light-off temperature than the calcined sample (CAT.1). It could be suggested that there was some precursor salt remained on the surface of the catalyst. Result in inhibited the catalytic activity for  $C_3H_8$  conversion. Whereas samples pretreated at higher temperature, from 300 - 700 °C, can shift the light-off temperature to a lower value (Figure 5.11). Until the pretreatment temperature of 600 °C (CAT. 22) was reached, it did not show any further improvement in light-off temperature compared to the pretreatment at 700 °C (CAT. 23).

The activity of catalysts for CO conversion (Figure 5.12) was found again that there wasn't any difference between all samples. The light-off temperature was around 175 °C as shown in Table 5.7. It may be suggested that the catalytic activity in removing CO for all samples were so high. Thus, the effect of pretreatment temperature on the catalytic activity could not be clearly observed.

The result obtained from propane conversion clearly show that the activity of the catalysts depended on the pretreatment temperature where the higher pretreatment temperature the higher activity. The orders of propane conversion are:

$$\text{CAT.23~CAT.22} > \text{CAT.9} > \text{CAT.7} > \text{CAT.5} > \text{CAT.1} > \text{CAT.21}$$

In the above result, even though CAT.5 has the lowest activity, it is still more than the activity of CAT.1. For this reason, the following study is chosen at 300 °C to be main pretreatment temperature. It should be noted here that too high pretreatment temperature many cause the catalyst to sinter. Therefore, this how pretreatment temperature was selected.

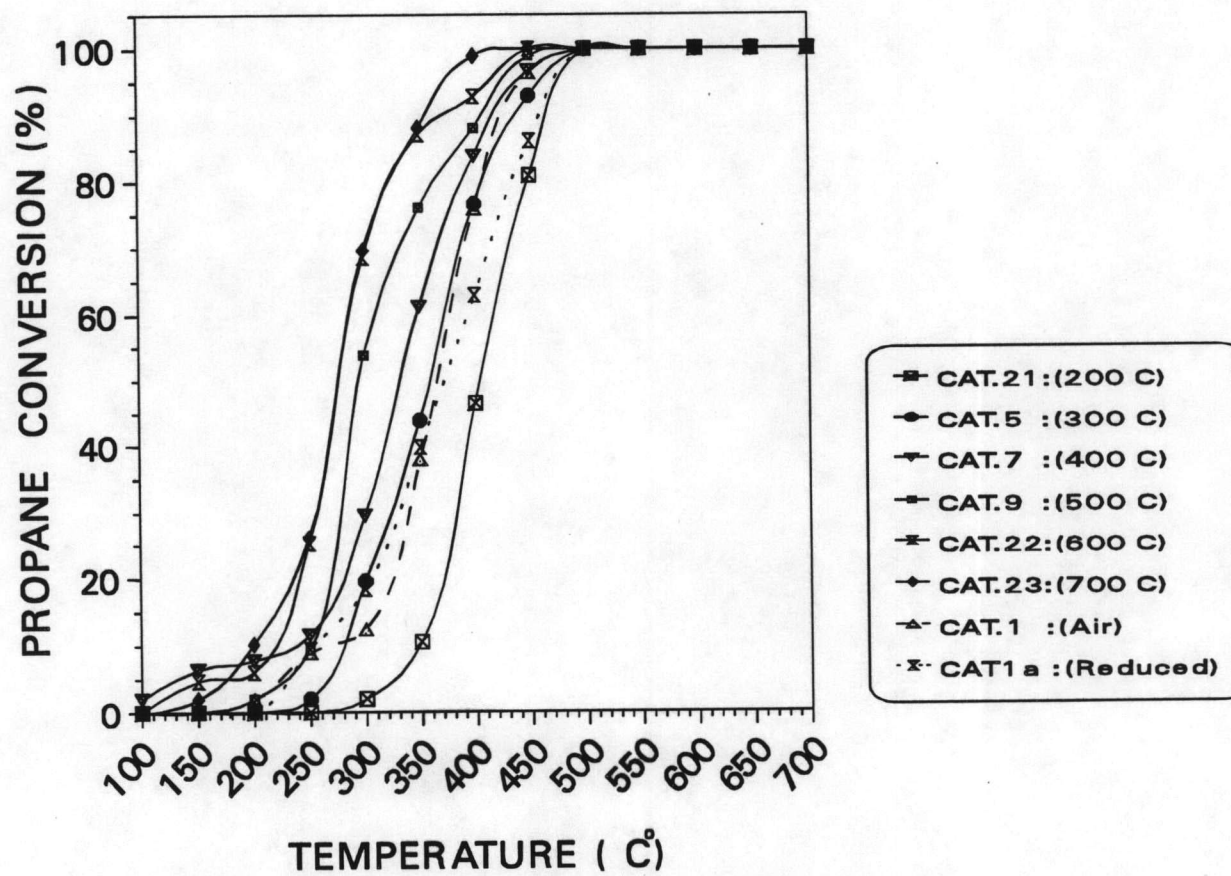


Figure 5.11 Effect of pretreatment temperature on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup>, S<sub>1</sub> = 0.8 Feed composition at excess O<sub>2</sub> (S<sub>2</sub> = 2.0)

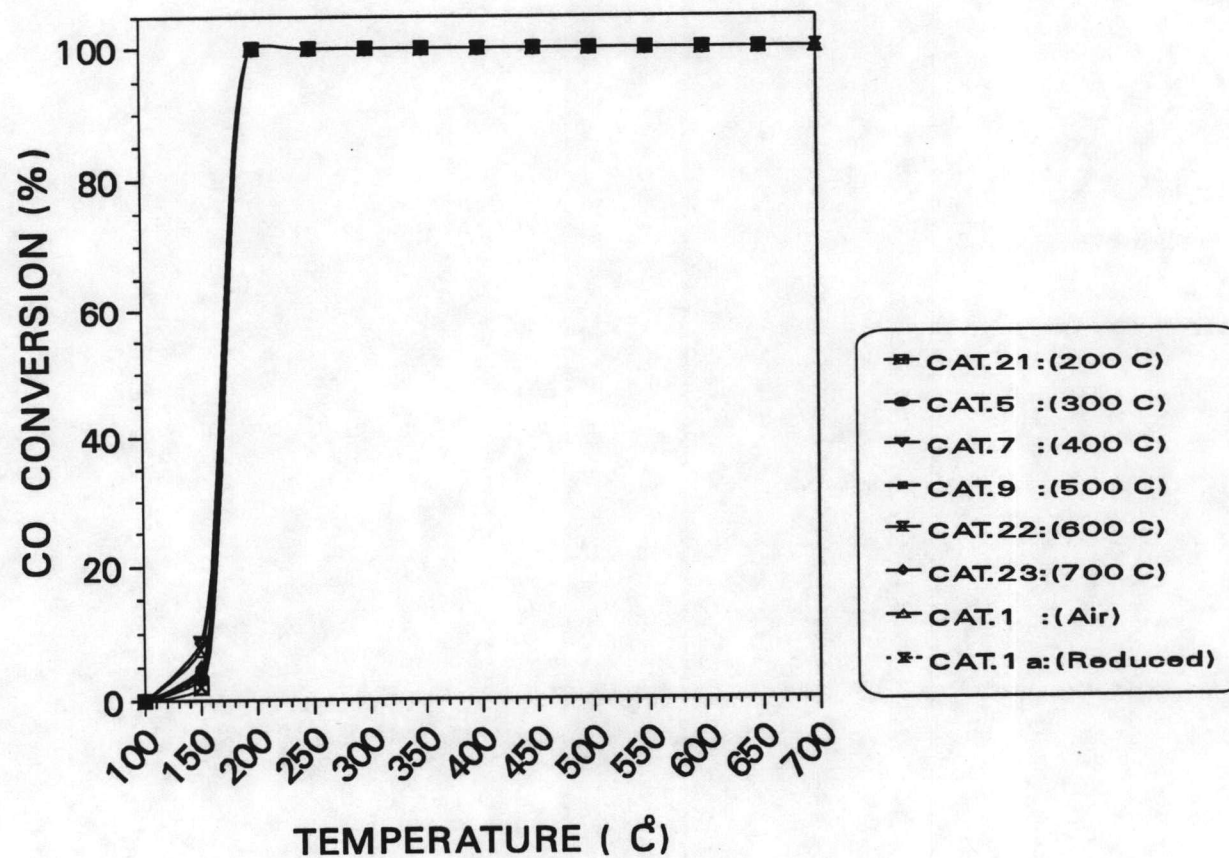


Figure 5.12 Effect of pretreatment temperature on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup>, S<sub>1</sub> = 0.8  
Feed composition at excess O<sub>2</sub> (S<sub>2</sub> = 2.0)

Table 5.7 The light-off temperature of catalyst pretreated in various pretreatment temperature.

Catalysts Name	Light-off Temperature(°C)	
	C <sub>3</sub> H <sub>8</sub> Conv.	CO Conv.
CAT.1	365	175
CAT.21	410	175
CAT.5	355	175
CAT.7	335	175
CAT.9	295	175
CAT.22	275	175
CAT.23	275	175

A possible reason that may be used to explain the enhancing in the catalytic activity is the form of active sites formed. In rich pretreatment condition part of Pt oxide may be reduced back to Pt metal while the rest remained Pt oxide. The existence of Pt oxide inhibited the sintering of Pt metal sites formed. Thus, Pt metal site were well dispersed. In reducing atmosphere, though, higher amount of Pt oxide were reduces to Pt metal this Pt cause to sinter to form larger metal sites. Therefore, in this latter case lower Pt metal surface area was formed resulting in lower catalytic activity. To prove this hypothesis, catalyst calcined in air at 500 °C (CAT.1) was reduced in 10% H<sub>2</sub> atmosphere at 500 °C for 2 hr (CAT.1a). It was found (Figure 5.11) that the light-off temperature of this catalyst for propane conversion was 370 °C which was higher than 295 °C of CAT.9, which was pretreated in rich condition at 500 °C for 2 hr. Therefore, it may be suggested that catalyst calcination in reducing atmosphere could not obviously increase catalytic activity.

Table 5.8 Effect of pretreatment temperature on the active sites and BET surface area of catalyst pretreated in rich condition ( $S_1 = 0.8$ ).

Catalyst	Active site (CO molecule/g.cat.)	BET (m <sup>2</sup> /g.cat)
CAT. 1	$5.11 \times 10^{17}$	288.27
CAT. 21	$4.81 \times 10^{17}$	264.69
CAT. 5	$3.25 \times 10^{17}$	252.10
CAT. 7	$1.28 \times 10^{17}$	255.44
CAT. 9	$1.26 \times 10^{17}$	257.83
CAT. 22	$0.68 \times 10^{17}$	259.00
CAT. 23	$0.65 \times 10^{17}$	244.11

The active site and BET surface area are shown in Table 5.8. It should be noted that the active site and BET surface area trend to decrease with increasing pretreatment temperature. Hence, it can be suggested that the catalytic activity depended on the pretreatment temperature. The increase in temperature can develop the efficiency and activity of the catalysts. The amount of adsorbed CO for all samples is shown in Figure 5.13. It is noted that when the pretreatment temperature was increased from 200-700 °C, the amount of adsorbed CO relatively decreased. The calcined catalyst (CAT.1) adsorbed the highest amount of CO, whereas the pretreated catalyst (CAT.19) adsorbed the lowest amount of CO but had the highest in the catalytic activity. This phenomenon may involve the Strong Metal Support Interaction (SMSI) effect. 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 [39].

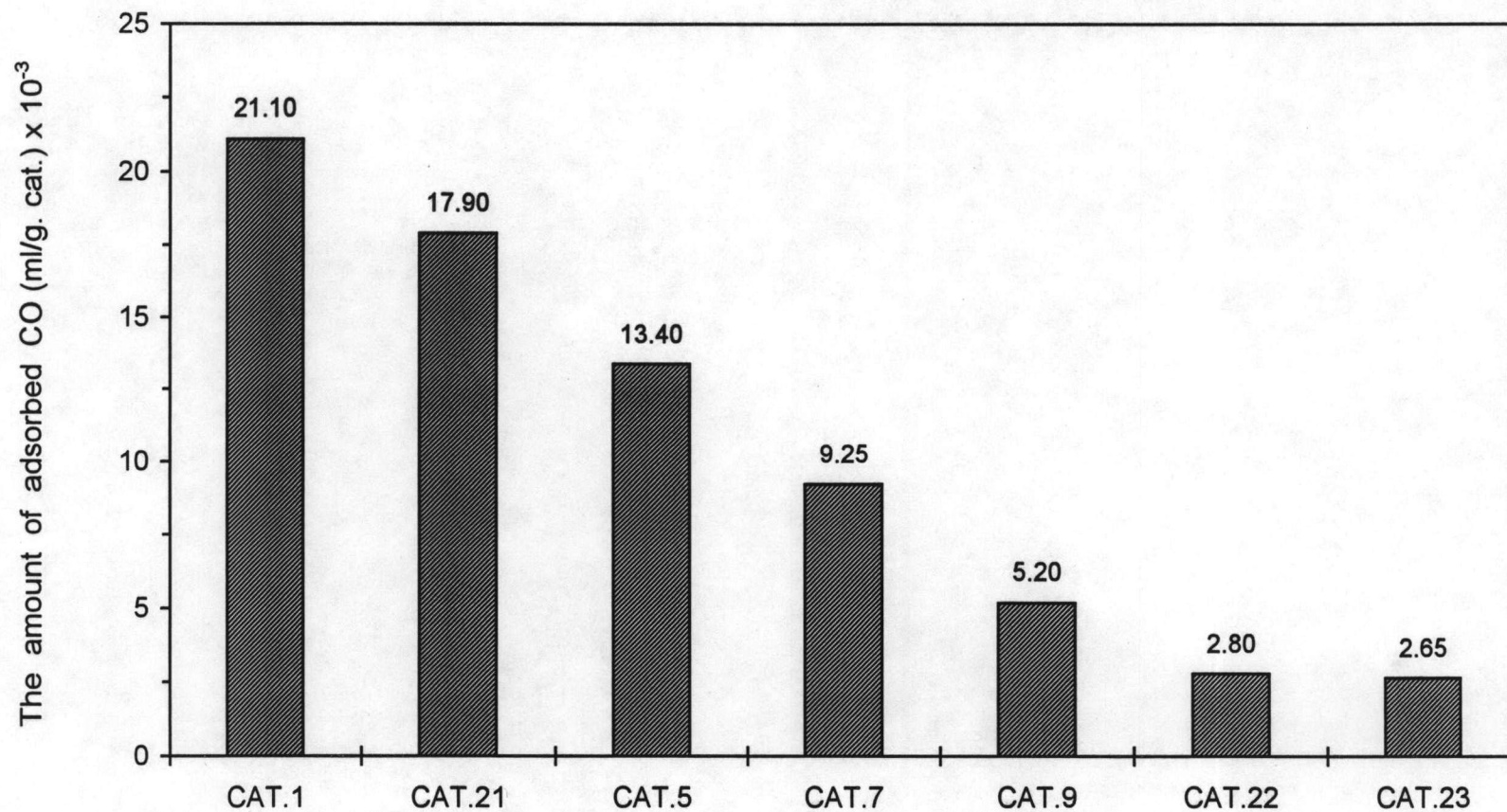


Figure 5.13 Effect of pretreatment temperature on the capacity of adsorbed CO by the pretreated catalysts.



Tauster [40] reported that SMSI phenomenon for supported metallic catalysts come from a reduction at elevated temperature which reduces the cations of the support to an oxidation state lower than its original state. The consequence of this interaction is a suppression of  $H_2$  and CO chemisorption of the supported metals but they usually do not lost their catalytic activity.

Another explanation for this increase in the catalytic activity when pretreatment temperature was increased, derived from the results of the  $CO_2$  adsorption technique. The procedure of this technique is similar to that of CO adsorption technique but different in the amount of  $CO_2$  used. In this case,  $CO_2$  0.7 ml was injected to the samples at room temperature. The amount of adsorbed  $CO_2$  between CAT.1 and CAT.19 is illustrated in Figure 5.14. It was found that CAT.19 (1.14 ml/g. cat. ) adsorbed a smaller amount of  $CO_2$  than CAT.1(1.5 ml/g. cat.). In other words, CAT.19 had the capacity to adsorbed  $CO_2$  24% decreased from CAT.1 which was relatively well to the better improvement in the light-off temperature about 25% between CAT.19 and CAT.1. It can be suggested that  $CO_2$  is the product of the CO and HC oxidation as shown in the reacting equations 3.3 and 3.4 in chapter III. Hence, the small amount of adsorbed  $CO_2$  on the catalyst surface may be caused the catalytic reaction shift toward the right side of the reaction. Result in the reactants were easily converted to be the products. That is to say, the lower amount of  $CO_2$  adsorbed on the surface of catalyst, the higher in the activity of initiating the catalytic reaction.

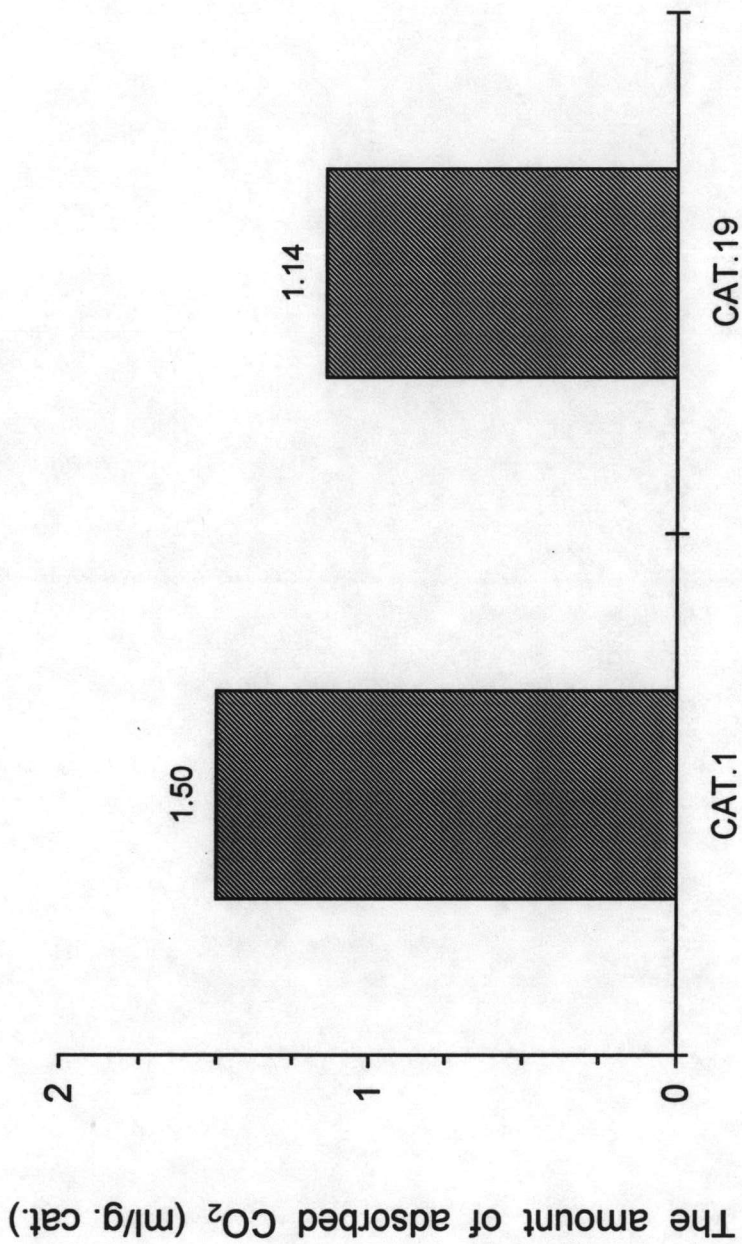


Figure 5.14 Comparison of the capacity of adsorbed CO<sub>2</sub> between calcined catalyst (CAT.1) and pretreated catalyst (CAT.19) by CO<sub>2</sub> adsorption technique

### 5.2.3 Effect of holding time on iso-thermal pretreatment

Catalysts were pretreated in various periods: 2, 5 and 10 hr. at a constant temperature of 500 °C in rich condition ( $S_1=0.8$ ) as shown in Table 5.9.

Table 5.9 Catalysts pretreated in various pretreatment time.

Name of Catalyst	Pretreatment Conditions
CAT. 1	Calcined in air at 500°C 4 hr.
CAT. 5	$S_1=0.8$ , 500°C, 2 hr.
CAT. 24	$S_1=0.8$ , 500°C, 5 hr.
CAT. 25	$S_1=0.8$ , 500°C, 10 hr.

Figure 5.15 shows the effect of increasing pretreatment time on propane conversion. It illustrates that propane conversion increased at 250 °C and reached the maximum conversion at 500 °C. Again, there was no any decrease of propane conversion at higher temperature. Increasing in pretreatment time from 2 to 10 hr. showed a slight increase in light-off temperature.

Figure 5.16 shows CO conversion of catalysts pretreated at different holding time. The conversion sharply increased between 150-200 °C without any decreased at higher temperature. There was no any differences in light-off temperature of all catalysts.

The light-off temperature of  $C_3H_8$  conversion (Figure 5.15) is slightly changed while the light-off temperature of CO conversion (Figure 5.16) is usually unchanged when pretreatment time is increased. That is to say, the catalytic activity doesn't depend on time consumed during pretreatment.

Table 5.10 Effect of pretreatment time on the active site and BET surface area of catalyst pretreated in rich condition ( $S_1 = 0.8$ ).

Catalyst	Pretreatment time (hr.)	Active site (CO molecule/g.cat.)	BET ( $m^2/g.cat$ )
CAT. 1	Calcined in air	$5.11 \times 10^{17}$	288.27
CAT. 5	2	$3.25 \times 10^{17}$	252.10
CAT. 24	5	$3.25 \times 10^{17}$	238.85
CAT. 25	10	$1.28 \times 10^{17}$	239.12

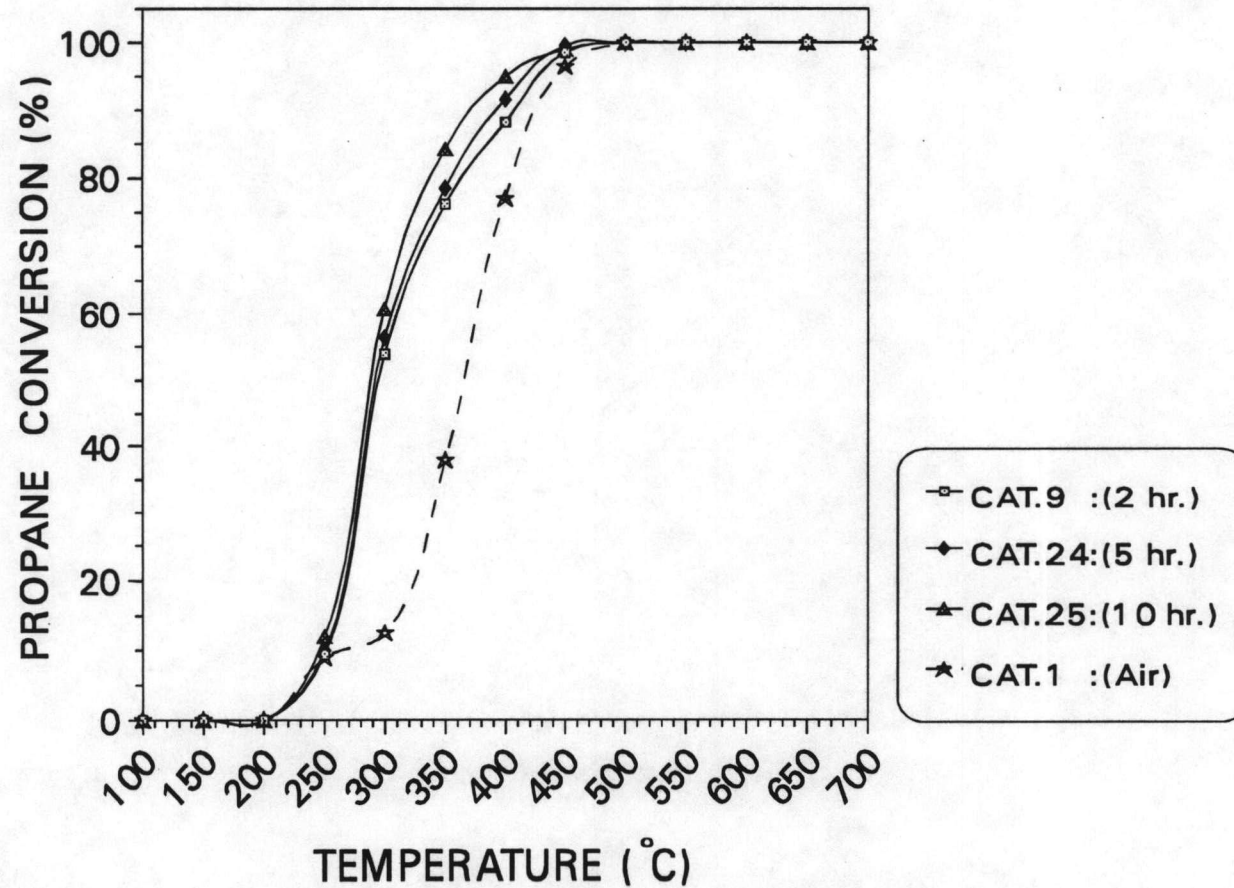


Figure 5.15 Effect of pretreatment time on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup>, S<sub>1</sub> = 0.8 Feed composition at excess O<sub>2</sub> (S<sub>2</sub> = 2.0)

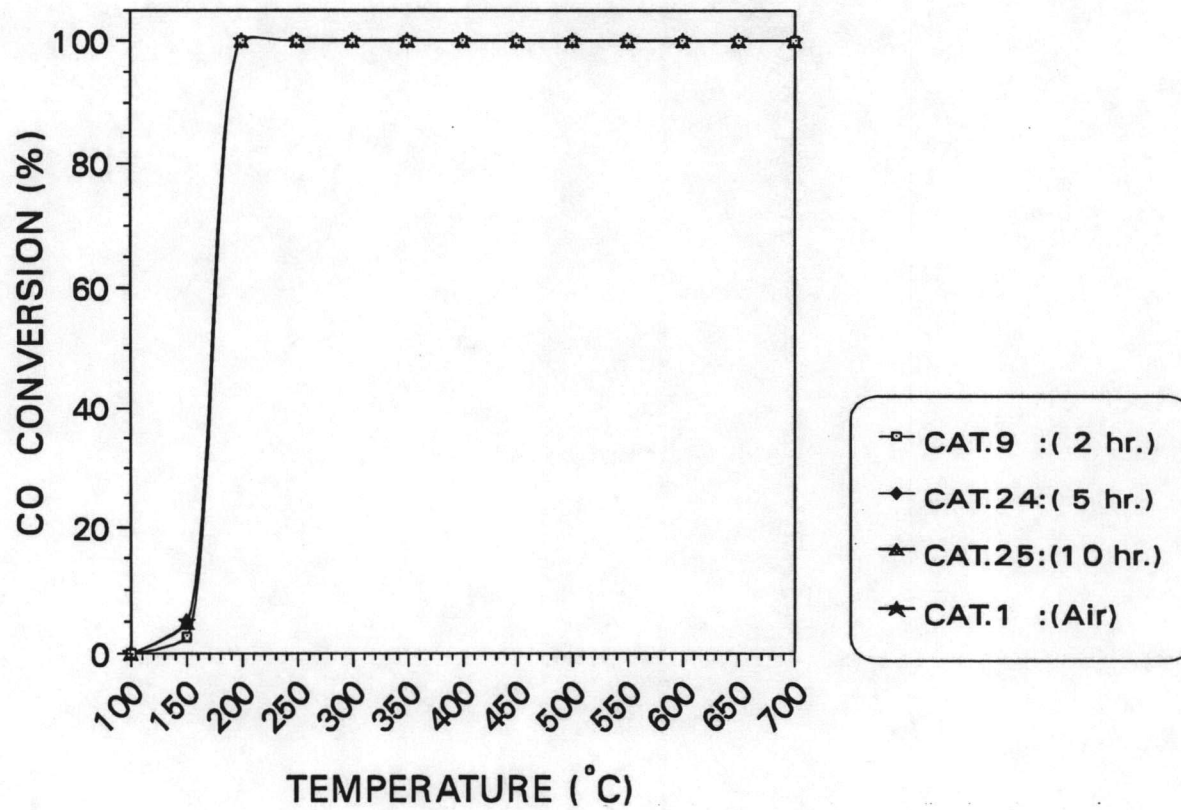


Figure 5.16 Effect of pretreatment temperature on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup>, S<sub>1</sub> = 0.8  
Feed composition at excess O<sub>2</sub> (S<sub>2</sub> = 2.0)

### 5.3 Catalytic Performance of Pt/Al<sub>2</sub>O<sub>3</sub> as Three-way Catalyst

The purpose of this part is aimed to study of the activity of Pt/Al<sub>2</sub>O<sub>3</sub> on exhaust gas removal in the same operation as a three-way catalyst by adding NO into gas mixtures. First, the study began with the effect of varying O<sub>2</sub> content in simulated exhaust gas for pretreated catalysts and ended with the effect of Air/Fuel ratio on NO, CO and propane conversion with catalyst prepared by procedure between calcination and pretreatment. The obtained experimental results are reported below.

#### 5.3.1 Effect of O<sub>2</sub> content on thermal pretreatment

Catalysts were pretreated for 2 hr. at 300 °C in gas mixtures which have various O<sub>2</sub> content as listed in Table 5.11. The catalysts were tested in stoichiometric gas composition between 150-700 °C.

Table 5.11 Catalysts pretreated in various O<sub>2</sub> content.

Name of Catalyst	Pretreatment Conditions
CAT. 26	calcined in air at 500°C 4 hr.
CAT. 27	S <sub>1</sub> =0.8, 300°C, 2 hr.
CAT. 28	S <sub>1</sub> =1.0, 300°C, 2 hr.
CAT. 29	S <sub>1</sub> =2.0, 300°C, 2 hr.

Figure 5.17 shows the effect of catalyst pretreated in simulated exhaust gas with varying oxygen content from rich to lean condition on NO to N<sub>2</sub> conversion. All conversion curves began to increase at 300 °C and

reached 80% maximum NO to N<sub>2</sub> conversion at 500 °C. The orders of curves raising up was the pretreated catalyst under rich, stoichiometric, and lean condition respectively. It was observed that the light-off temperatures of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst which was pretreated under rich and stoichiometric conditions were slightly different. But when this Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was pretreated in lean condition, it showed higher light-off temperature than pretreatment in rich or stoichiometric conditions.

Figure 5.18 shows that the propane conversion began to increase at 300 °C and reached 100% maximum conversion at 450 °C. The order of conversion raising up was the same as NO to N<sub>2</sub> conversion which the conversion of catalyst pretreated under rich condition raised up first, followed by catalysts pretreated at stoichiometric and lean condition respectively. The slightly increase in light-off temperature was observed when increasing O<sub>2</sub> content in pretreatment exhaust gas.

Figure 5.19 shows that CO conversion sharply increased when the reaction temperature was raised up from 200 to 300 °C. The only exception is the catalyst pretreated in lean condition which CO conversion began to increase at 250 °C and reached the maximum conversion at 350 °C.

From the experimental results it was found that the catalysts pretreated in rich (CAT. 27) and stoichiometric (CAT. 28) condition have lower light-off temperature for NO to N<sub>2</sub> conversion (Figure 5.17) than the catalyst calcined in air (CAT. 26) as shown in Table 5.12.



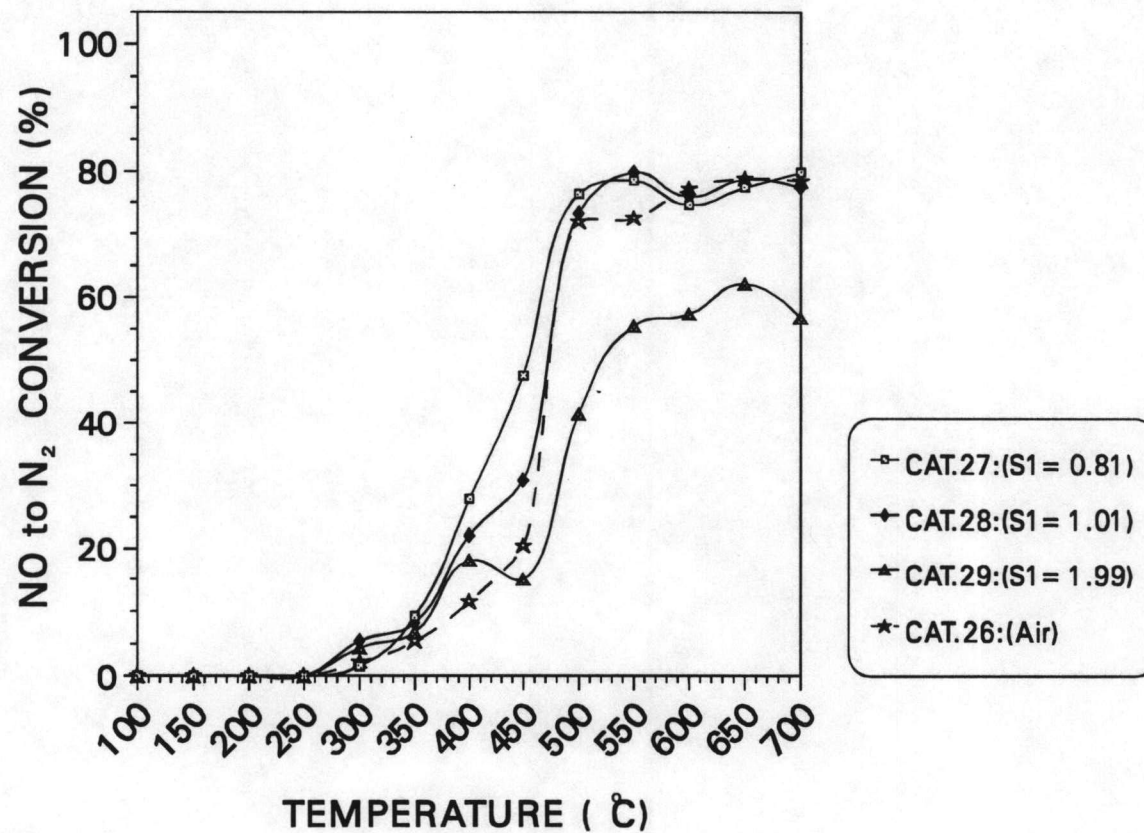


Figure 5.17 Effect of O<sub>2</sub> content on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for NO Conversion, GHSV = 15,000 h<sup>-1</sup>  
Feed composition at stoichiometric (S<sub>2</sub> = 1.0)

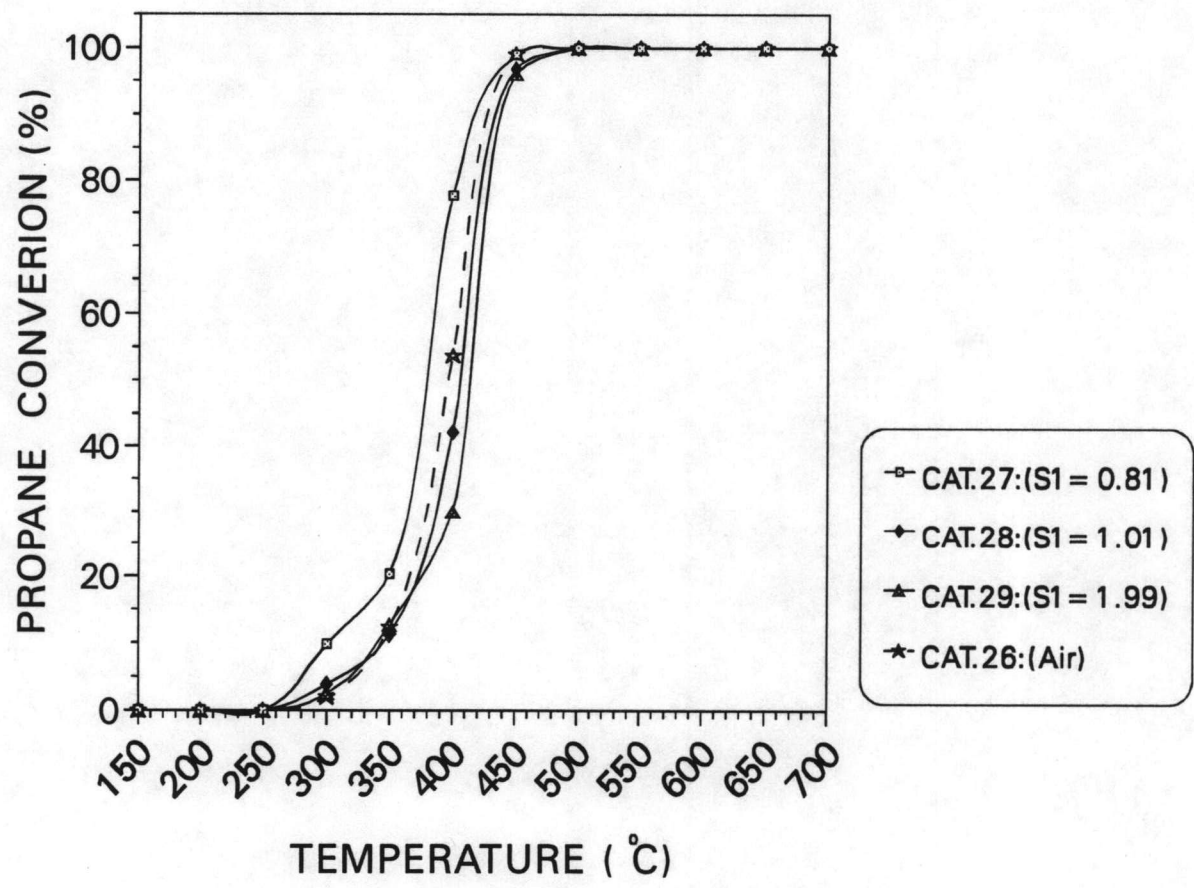


Figure 5.18 Effect of O<sub>2</sub> content on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup> Feed composition at stoichiometric (S<sub>2</sub>= 1.0)

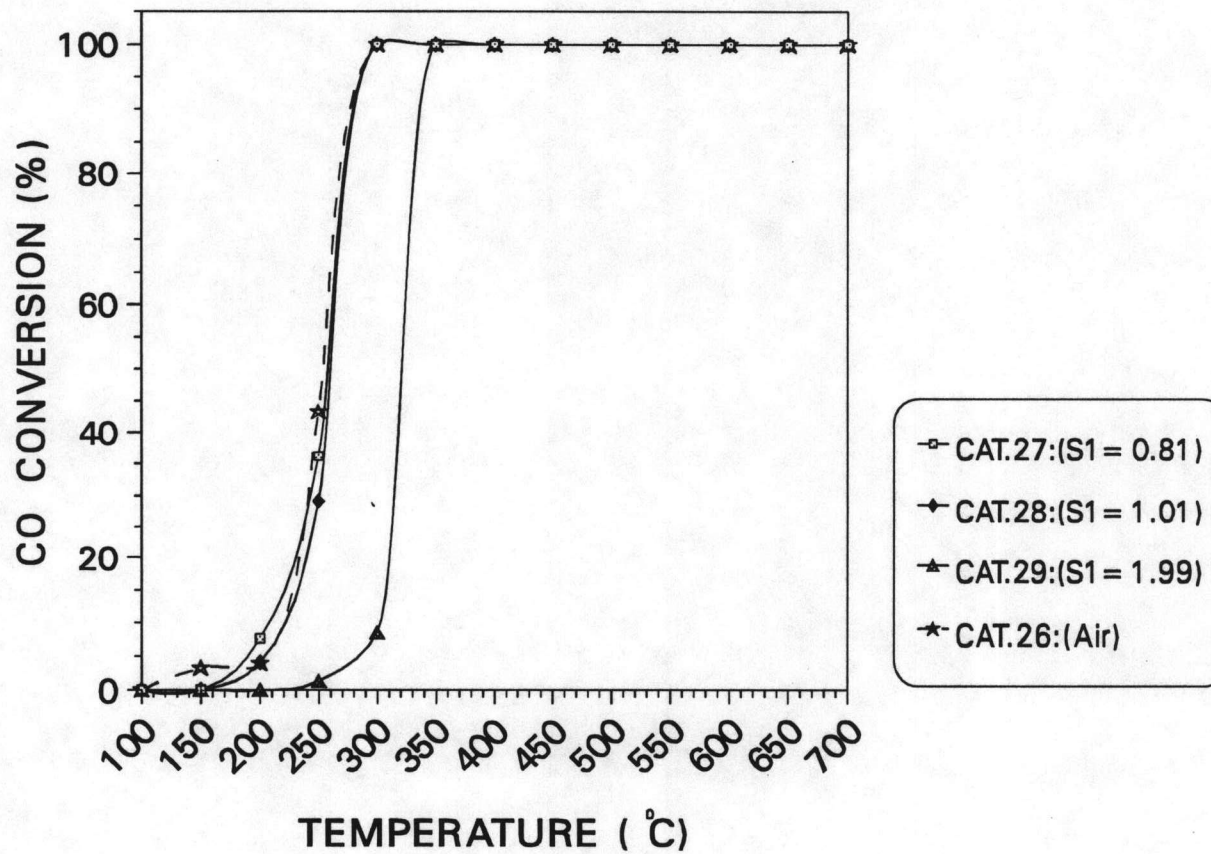


Figure 5.19 Effect of O<sub>2</sub> content on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup>  
Feed composition at stoichiometric (S<sub>2</sub>= 1.0)

Table 5.12 Shown the light-off temperature of catalysts pretreated in various O<sub>2</sub> content.

Catalysts Name	Light-off Temperature (°C) of		
	NO Conv.	C <sub>3</sub> H <sub>8</sub> Conv.	CO Conv.
CAT.26	470	395	255
CAT.27	425	380	255
CAT.28	455	405	260
CAT.29	500	415	320

For C<sub>3</sub>H<sub>8</sub> conversion (Figure 5.18), CAT.27 still has better activity than CAT.26 which was observed to have a lower light-off temperature. Furthermore, it was observed that the catalysts pretreated in stoichiometric (CAT.28) and lean (CAT.29) conditions did not show any improvement in their catalytic activity.

The result of CO conversion (Figure 5.19), shows that there were no difference among light-off temperatures of CAT.26, CAT.27, and CAT.28. But for the catalyst pretreated in lean gas mixtures (CAT.29), it was obvious that the activity was lower. Its light-off temperature is about 70 °C higher. The explanation for this may be the excess O<sub>2</sub> in the reactant mixtures that inhibited the removal of precursor salts from the surface of the catalysts, result in decreasing of the activity of catalyst.

### 5.3.2 Effect of Air/Fuel ratio on Catalytic Performance

This experiment involves an investigation of the conversion efficiency of CO, NO and propane as a function of stoichiometric number. The activity of catalysts in various gas compositions were measured at 500 °C. The gas compositions are characterized by the stoichiometric number (S).

Figure 5.20 shows the effect of varying O<sub>2</sub> content in the reactant gas for pretreated and calcined catalyst. From rich to stoichiometric region, NO to N<sub>2</sub> conversion maintained at 80% conversion while CO and C<sub>3</sub>H<sub>8</sub> conversion slightly increased relatively to the increase of O<sub>2</sub> content in the reactant gas. CO and C<sub>3</sub>H<sub>8</sub> conversions reached 100% maximum conversion at stoichiometric point (S=1.0). From stoichiometric to lean region, NO to N<sub>2</sub> conversion sharply decreased conversely to the increase of O<sub>2</sub> content. Whereas, CO and C<sub>3</sub>H<sub>8</sub> still maintained at 100% conversion.

It should be noted here that the catalyst should essentially operate as close to the stoichiometric point as possible in order to effectively convert simultaneously all the pollutants as illustrated in Figure 5.20. In the rich region, the limiting factor is the CO and propane conversion. While, in the lean region, it is the NO conversion. As can be seen in Figure 5.20, the catalyst pretreated in rich simulated exhaust gas (CAT.27) has higher performance for all CO, NO and propane conversion than the conventional platinum catalyst (CAT.27). It can be indicated in term of 'window'. The definition of window here is the Air/Fuel range that could be convert all pollutants more than 80% conversion[27]. The window of CAT.26 can be defined as  $1 \pm 0.02$  whereas CAT.27 can be broadly defined as  $1 \pm 0.025$ .

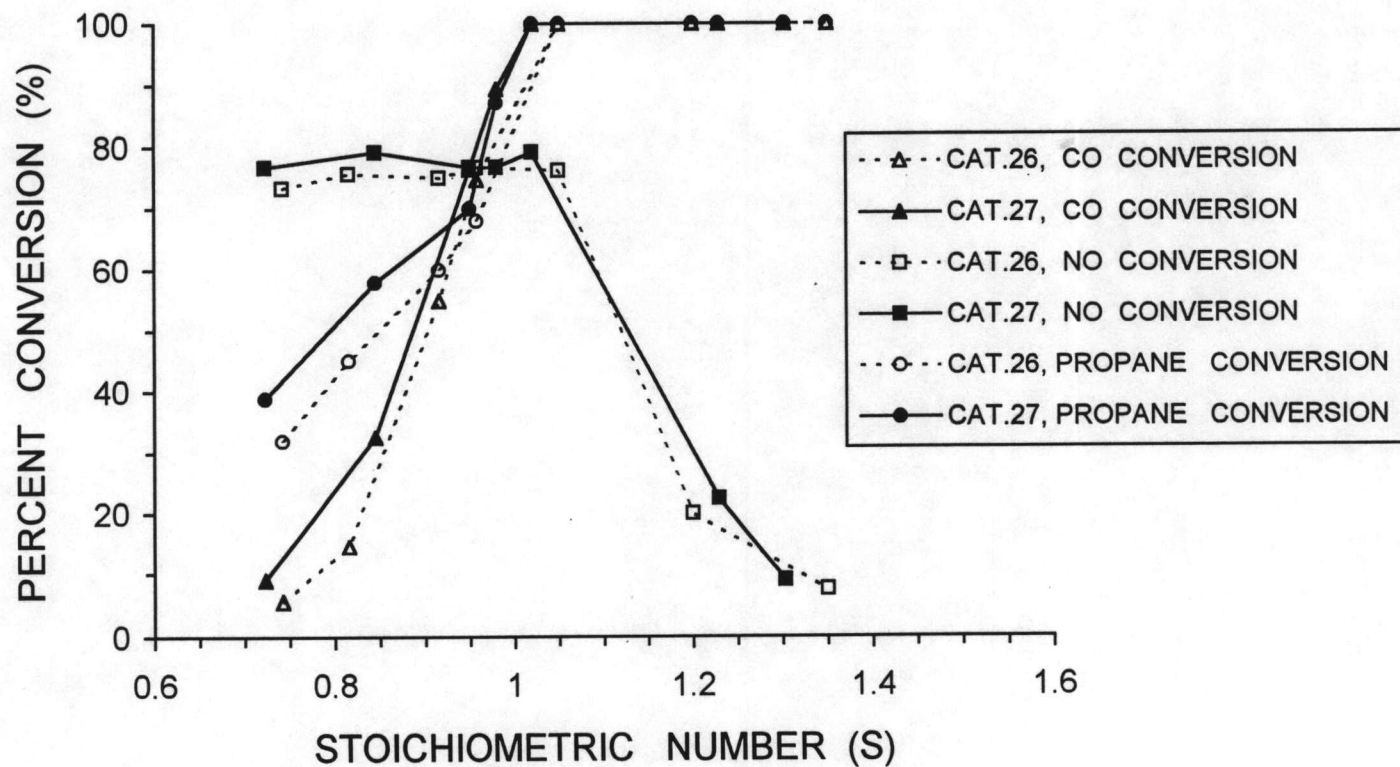


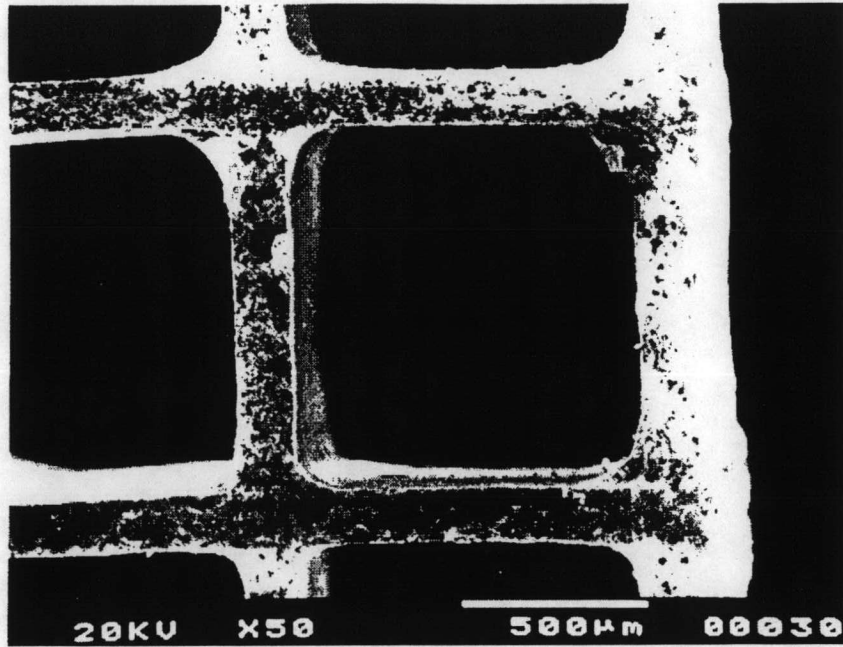
Figure 5.20 Effect of Air/Fuel Ratio on CAT.26 and CAT.27 for NO, CO and Propane Conversion of at 500 °C, GHSV = 15,000 h<sup>-1</sup>

## 5.4 Catalytic Performance of Platinum Supported on Washcoat Monolithic Catalyst

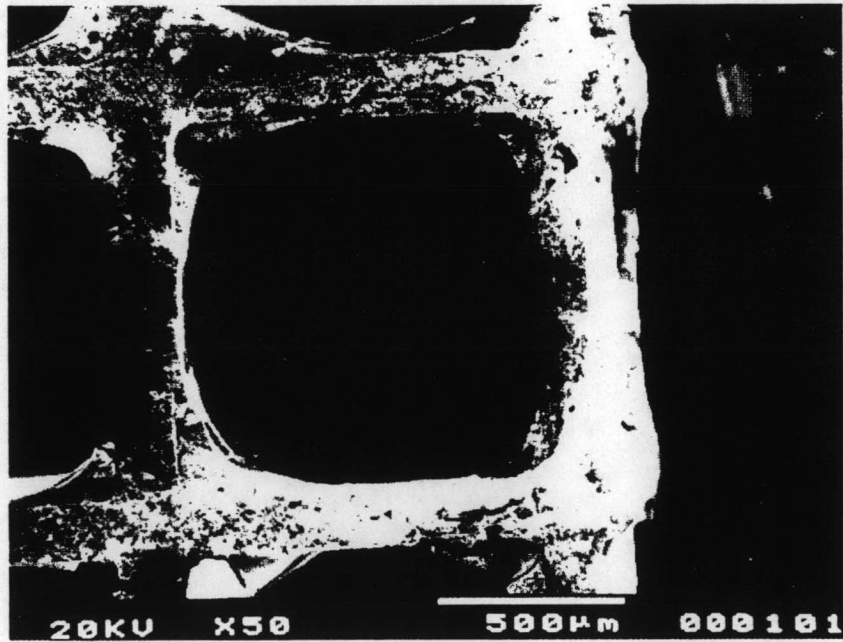
The purpose of this section is to study the behavior of catalyst on CO, C<sub>3</sub>H<sub>8</sub> and NO conversions by platinum supported on washcoat monolith. The test samples used had a bar cordierite honeycomb structure (400 cell/in<sup>2</sup>), 3 mm (W) x 3 mm (H) x 20 mm (L). SEM photographs of this monolithic honeycomb are illustrated in Figure 5.21 which show pore structure before and after coating with alumina powder in horizontal (Figures 5.21a and b.) and vertical (Figures 5.21c and d.) cross sectional area. The study started with varying pretreatment conditions from rich to stoichiometric and lean conditions. After that, the effect of varying pretreatment temperature is investigated. Finally, the effect of Air/Fuel ratio on the catalytic activity is studied. The testing gas mixtures is kept near the stoichiometric composition ( $S_2=1.0$ ) and the reaction took place between 150-700°C.

### 5.4.1 Effect of O<sub>2</sub> content on thermal pretreatment

Catalyst samples were pretreated at 300 °C for 2 hr. in various gas mixtures as shown in Table 5.13. The catalytic activities for CO, C<sub>3</sub>H<sub>8</sub>, and NO to N<sub>2</sub> conversion at the temperature ranging of 150-700 °C were observed.



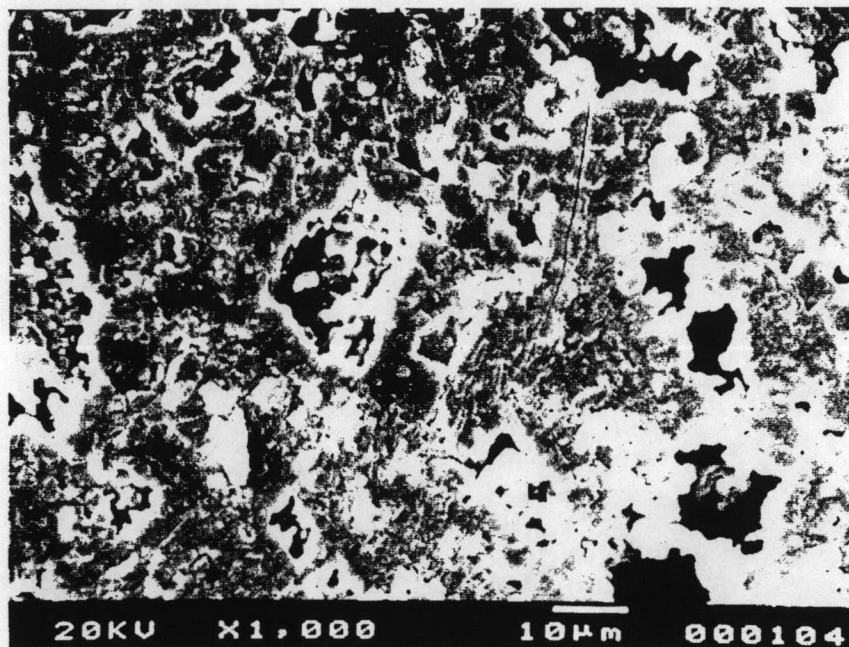
a.) Before coating (Horizontal cross-section)



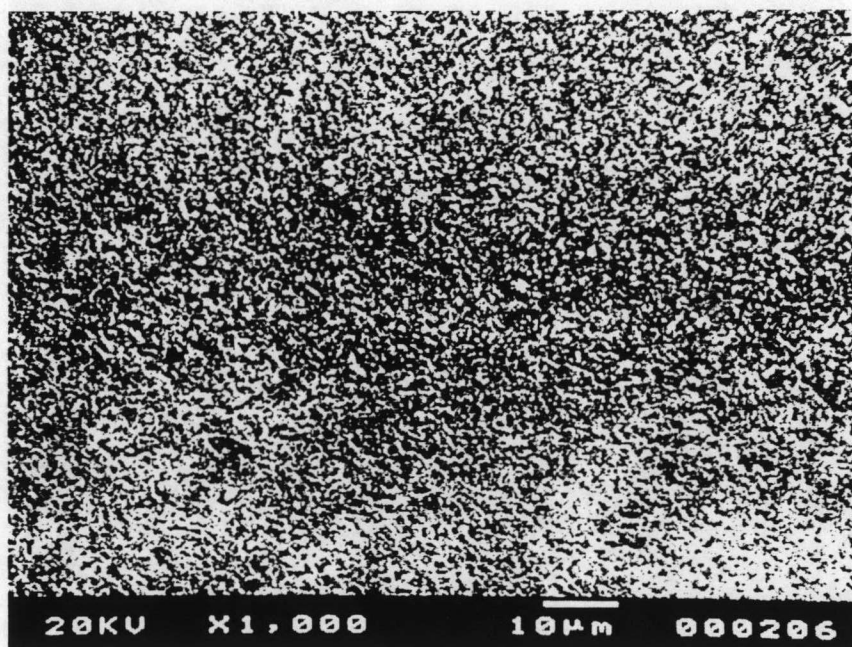
b.) After coating (Horizontal cross-section)

Figure 5.21 SEM photographs of monolithic honeycomb pore structure





c.) Before coating (Vertical cross-sectional)



d.) After coating (Vertical cross-sectional)

Table 5.13 Pt on monolithic catalysts pretreated in various O<sub>2</sub> content.

Name of Catalyst	Pretreatment Conditions
CAT.30	calcined in air at 500°C 4 hr.
CAT.31	S <sub>1</sub> =0.8, 300°C, 2 hr.
CAT.32	S <sub>1</sub> =1.0, 300°C, 2 hr.
CAT.33	S <sub>1</sub> =2.0, 300°C, 2 hr.

Figure 5.22 shows the effect of varying O<sub>2</sub> content in pretreatment exhaust gas for Pt supported on washcoat monolithic catalysts. The similar trend can be seen in NO conversion on Pt supported on alumina support which showed that the NO conversion began to increase at 300 °C and reached 80% maximum conversion at 500 °C. The order of conversion curve raising up was the catalyst pretreated under rich, stoichiometric, and lean condition respectively.

Figure 5.23 shows that C<sub>3</sub>H<sub>8</sub> conversion of the catalyst pretreated under rich condition began to increase at 250 °C and reached the maximum conversion at 400 °C without any decrease at higher temperature. The similar trend was observed for the other catalysts.

Figure 5.24 shows that CO conversion of all samples sharply increased between 200-300 °C. There was a slight difference in light-off temperature between pretreated catalysts which a pretreated catalyst under rich condition gave the lowest light-off temperature.

At first, the NO to N<sub>2</sub> conversion (Figure 5.22) was considered. Catalyst pretreated in rich condition (CAT.31) gave the lowest light-off temperature (about 430 °C), followed by CAT.32 (460 °C), CAT.30 (480 °C) and CAT.33 (560 °C). All samples reached their maximum conversions in high temperature region (600-700 °C). The light-off temperatures of all catalysts are summarized in Table 5.14.

Table 5.14 Shown the light-off temperature of catalysts pretreated in various O<sub>2</sub> content.

Catalysts Name	Light-off Temperature(°C) of		
	NO Conv.	C <sub>3</sub> H <sub>8</sub> Conv.	CO Conv.
CAT.30	480	330	270
CAT.31	430	305	230
CAT.32	460	320	245
CAT.33	560	340	245

The effect of varying pretreatment condition on C<sub>3</sub>H<sub>8</sub> conversion is illustrated in Figure. 5.23. The results are similar to the activity of NO to N<sub>2</sub> conversion that the catalyst pretreated in simulated exhaust gas could improve its catalytic activity if the pretreatment condition was kept in stoichiometric or rich region. The catalyst pretreated in lean condition (CAT.33), however, did not show any improvement and similar result was observed in CO conversion (Figure 5.24).

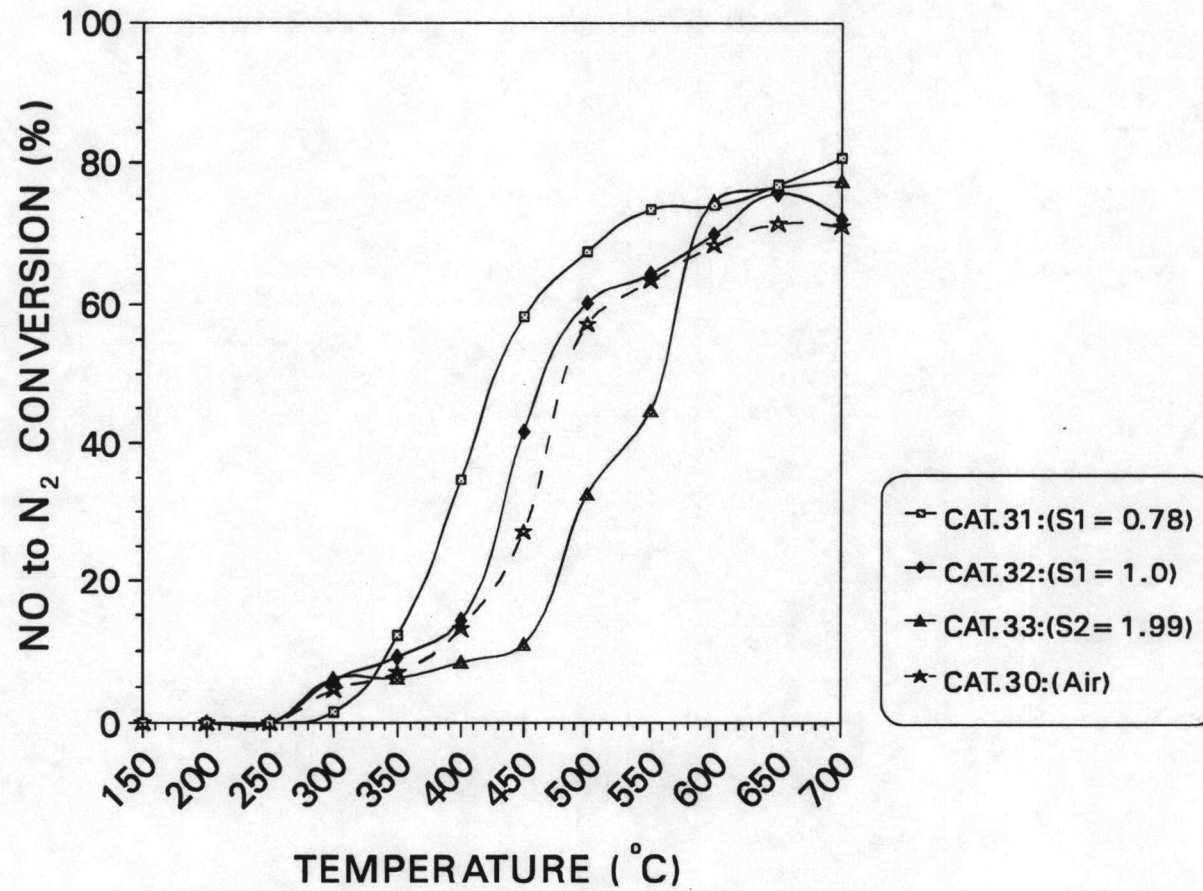


Figure 5.22 Effect of O<sub>2</sub> content in pretreatment on monolithic catalysts for NO Conversion, GHSV = 15,000 h<sup>-1</sup>  
Feed composition at stoichiometric (S<sub>2</sub> = 1.0)

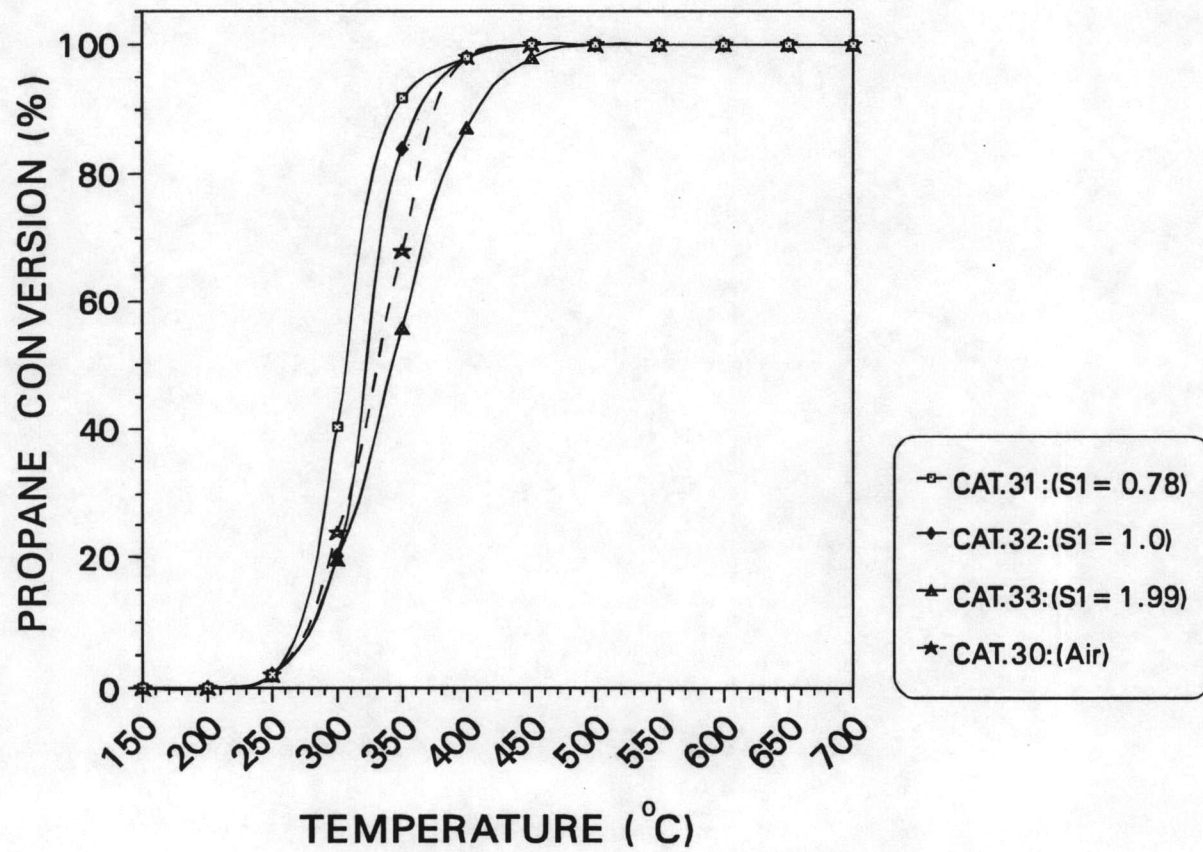


Figure 5.23 Effect of O<sub>2</sub> content in pretreatment on monolithic catalysts for Propane Conversion, GHSV = 15,000 h<sup>-1</sup> Feed composition at stoichiometric (S<sub>2</sub> = 1.0)

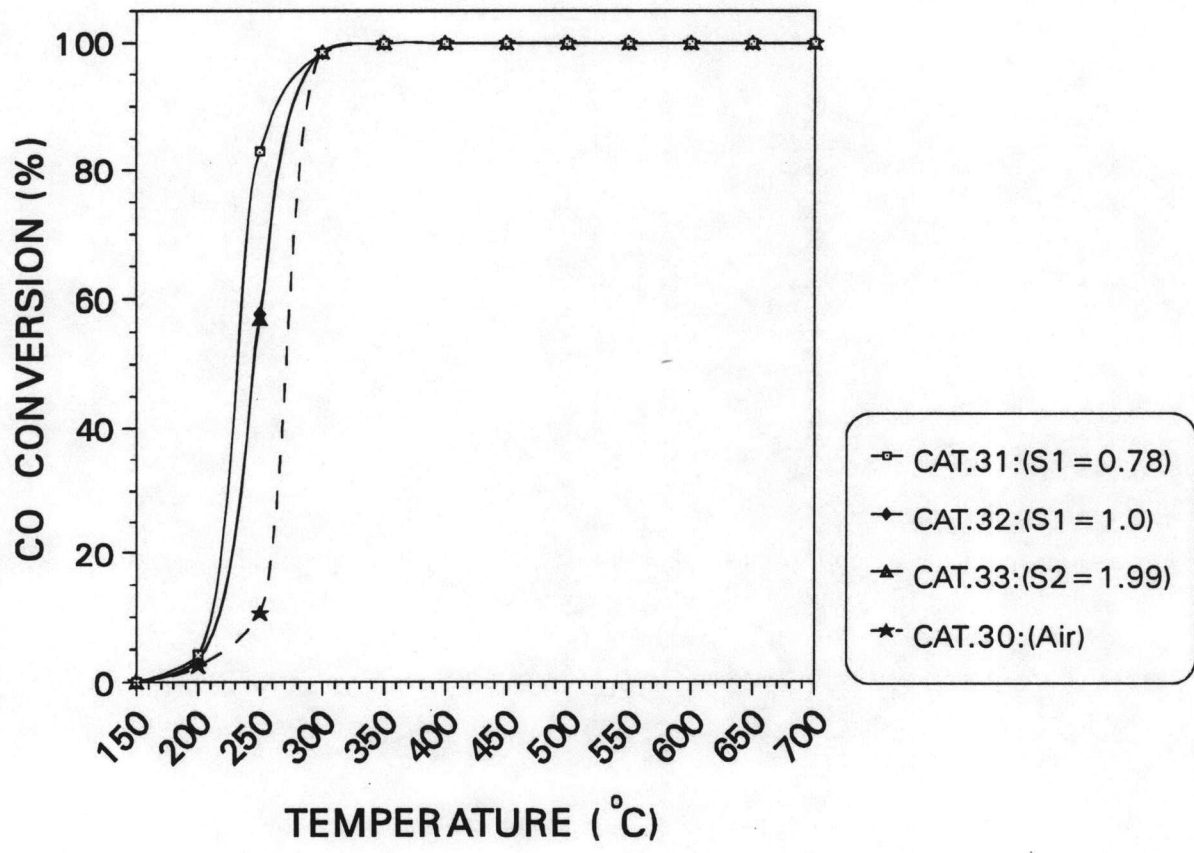


Figure 5.24 Effect of O<sub>2</sub> content in pretreatment on monolithic catalysts for CO Conversion, GHSV = 15,000 h<sup>-1</sup>  
Feed composition at stoichiometric (S<sub>2</sub>= 1.0)



The orders of catalytic activity of all the reactions were:

NO to N<sub>2</sub> conversion:

CAT.31 > CAT.32 > CAT.30 > CAT.33

C<sub>3</sub>H<sub>8</sub> conversion:

CAT.31 > CAT.32 > CAT.30 > CAT.33

CO conversion:

CAT.31 > CAT.32 ~ CAT.33 > CAT.30

The above results clearly show that the catalyst pretreated in rich condition (CAT.31) was still more active than the others.

#### 5.4.2 Effect of temperature on thermal pretreatment

The catalysts were pretreated in a rich gas mixture ( $S_1=0.8$ ) for 2 hr. at 300, 400, and 500°C as listed in Table 5.15. The prepared catalysts were investigated in stoichiometric gas mixtures ( $S_2=1.0$ ).

Table 5.15 Pt on monolithic catalysts pretreated in various pretreatment temperature.

Name of Catalyst	Pretreatment Conditions
CAT.30	calcined in air at 500°C 4 hr.
CAT.31	$S_1=0.8$ , 300°C, 2 hr.
CAT.34	$S_1=0.8$ , 400°C, 2 hr.
CAT.35	$S_1=0.8$ , 500°C, 2 hr.

Figure 5.25 shows the effect of pretreatment temperature in the range 300-500 °C on NO to N<sub>2</sub> conversion. The conversion curves increased at 300 °C and reached 80% maximum conversion at 500 °C. Furthermore, the conversion did not show any decrease in the conversion of NO at temperature higher than 500 °C. There was a slight decrease in light-off temperature with increasing pretreatment temperature.

Figure 5.26 shows that propane conversion began to increase at 250 °C and reached 100% maximum conversion at 400 °C. At further high temperature, the conversion maintained at this value.



Figure 5.27 shows that CO conversion sharply increased when the reaction temperature was raised from 200 to 300 °C. Again, there was no any conversion drop at high temperature. There was a slight decrease in light-off temperature when the pretreatment temperature was increased from 300-500 °C.

The results observed from NO, C<sub>3</sub>H<sub>8</sub> and CO conversion (Figure 5.25, 5.26, and 5.27) show that increasing pretreatment temperature has little advantage in catalytic activity. It could be suggested that there was a slight increase in light-off temperature when pretreatment temperature was increased. In other words, the activity of platinum supported on washcoat monolithic catalyst did not clearly depend on pretreatment temperature as much as that of platinum supported on alumina catalyst. It may be suggested that the experiments were carried out at low GHSV which all catalysts could achieve high conversion. Thus, the effect of pretreatment temperature on the activity of monolithic catalysts could not be clearly observed.

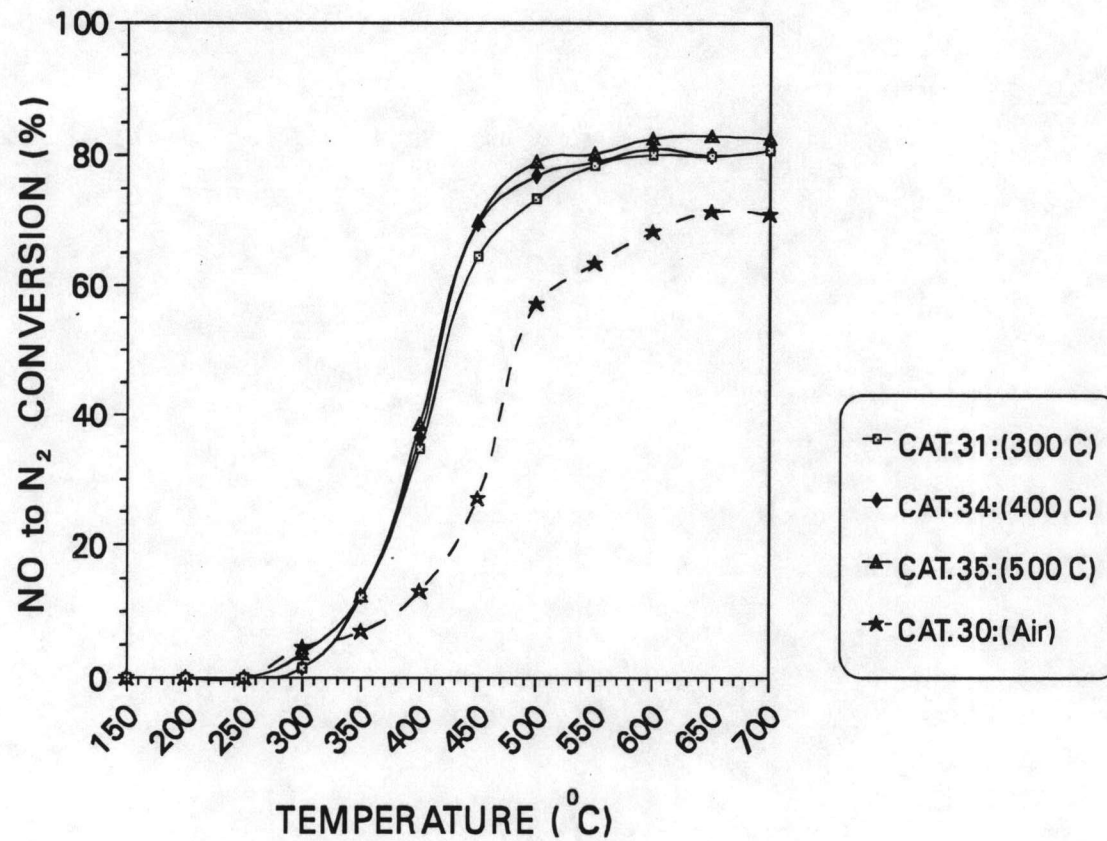


Figure 5.25 Effect of pretreatment time on monolithic catalysts for NO Conversion, GHSV = 15,000 h<sup>-1</sup>, S<sub>1</sub> = 0.8 Feed composition at stoichiometric (S<sub>2</sub> = 1.0)

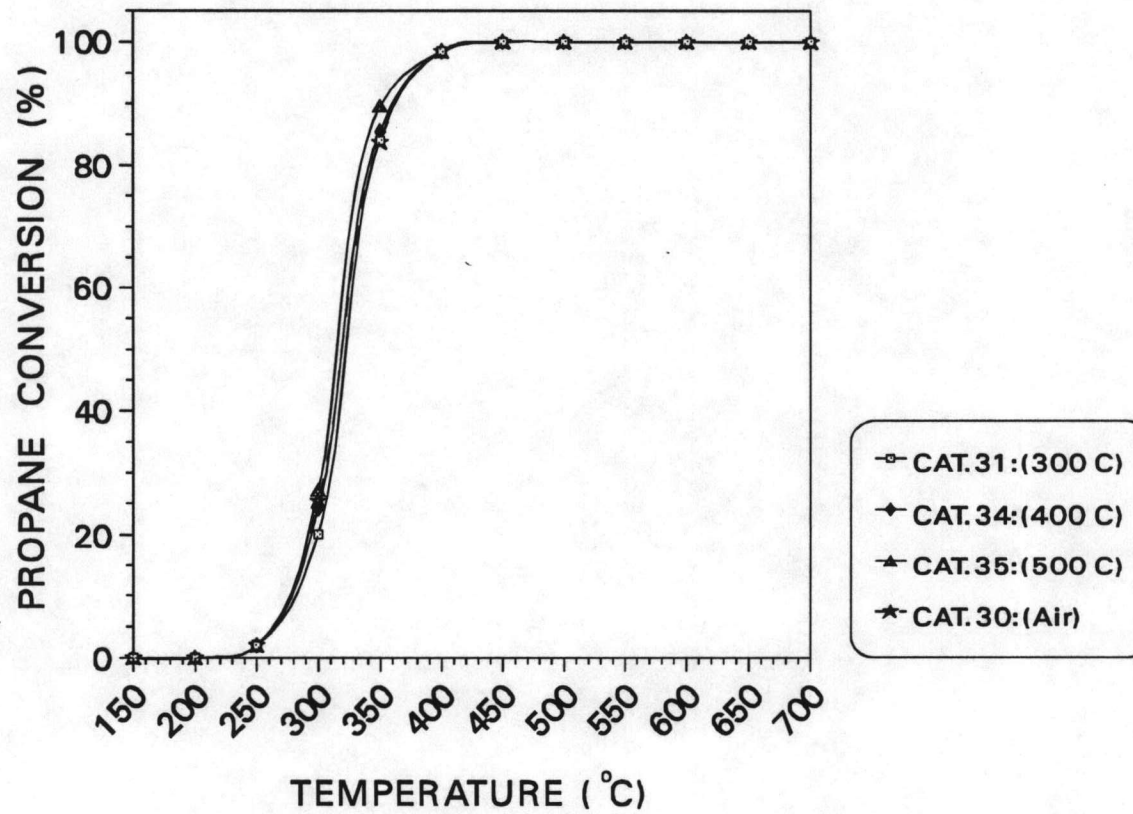


Figure 5.26 Effect of pretreatment time on monolithic catalysts for Propane Conversion,  $GHSV = 15,000 \text{ h}^{-1}$ ,  $S_1 = 0.8$  Feed composition at stoichiometric ( $S_2 = 1.0$ )

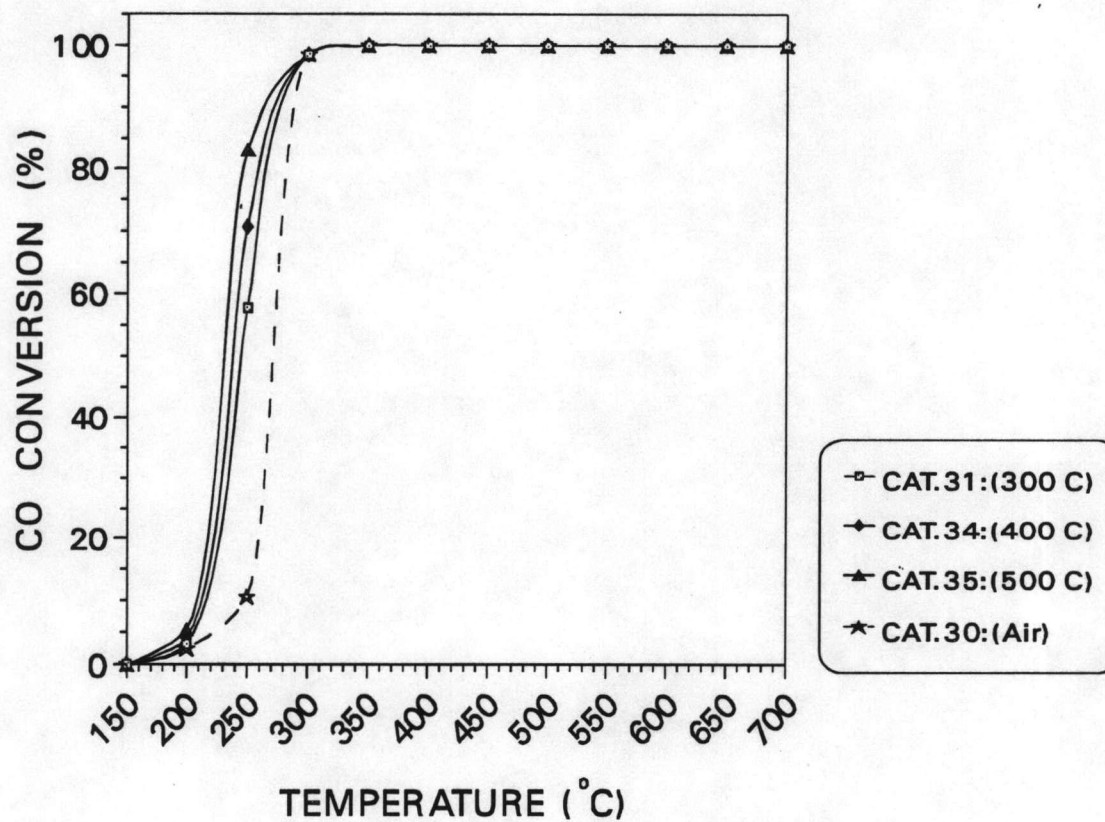


Figure 5.27 Effect of pretreatment time on monolithic catalysts for CO Conversion,  $GHSV = 15,000 \text{ h}^{-1}$ ,  $S_1 = 0.8$   
Feed composition at stoichiometric ( $S_2 = 1.0$ )

#### 5.4.3 Effect of Air/fuel ratio on catalytic performance.

The effect of oxygen content on the three-way catalyst is considered for platinum supported on washcoat monolith catalyst. The investigation is examined in the same procedure, which has been explained in the previous section for platinum supported on alumina catalyst, i.e. 500 °C and vary O<sub>2</sub> content. The CO, NO and propane conversion are plotted as a function of stoichiometric number (S) as shows in Figure 5.28.

Figure 5.28 shows the effect of Air/fuel ratio on the activity of pretreated and calcined catalysts at 500 °C. From rich to stoichiometric region, NO to N<sub>2</sub> conversion was maintained at 80% maximum conversion. While CO and C<sub>3</sub>H<sub>8</sub> conversion slightly increased when O<sub>2</sub> content in the reactant gas was increased. Until stoichiometric point was reached, NO conversion began to decrease. Whereas, both CO and C<sub>3</sub>H<sub>8</sub> conversion reached their 100% conversion. From stoichiometric to lean condition, NO conversion sharply decreased while CO and C<sub>3</sub>H<sub>8</sub> conversion still maintained at their maximum conversions.

The results show that under a slightly oxidizing atmosphere, the NO conversion sharply decreased while CO and propane conversion still maintain in the high level. In the rich condition, the NO conversion is relatively stable at a high level while the CO and propane conversion slightly decrease with the Stoichiometric No.(S).

The similar catalytic performance was observed on the catalyst pretreated in rich simulated exhaust gas (CAT.31) which showed higher catalytic activity for all CO, NO and propane conversion than the catalyst calcined in air (CAT.30), even though the support structure of catalyst was

changed. The window of CAT.30 can be defined as  $1 \pm 0.01$  whereas that of CAT.31 can be defined as  $1 \pm 0.015$ . As a result, the operating window of platinum supported on washcoat monolith is less in range than that supported on alumina. The explanation of these difference in windows may be the change from reaction control to pore diffusion control.

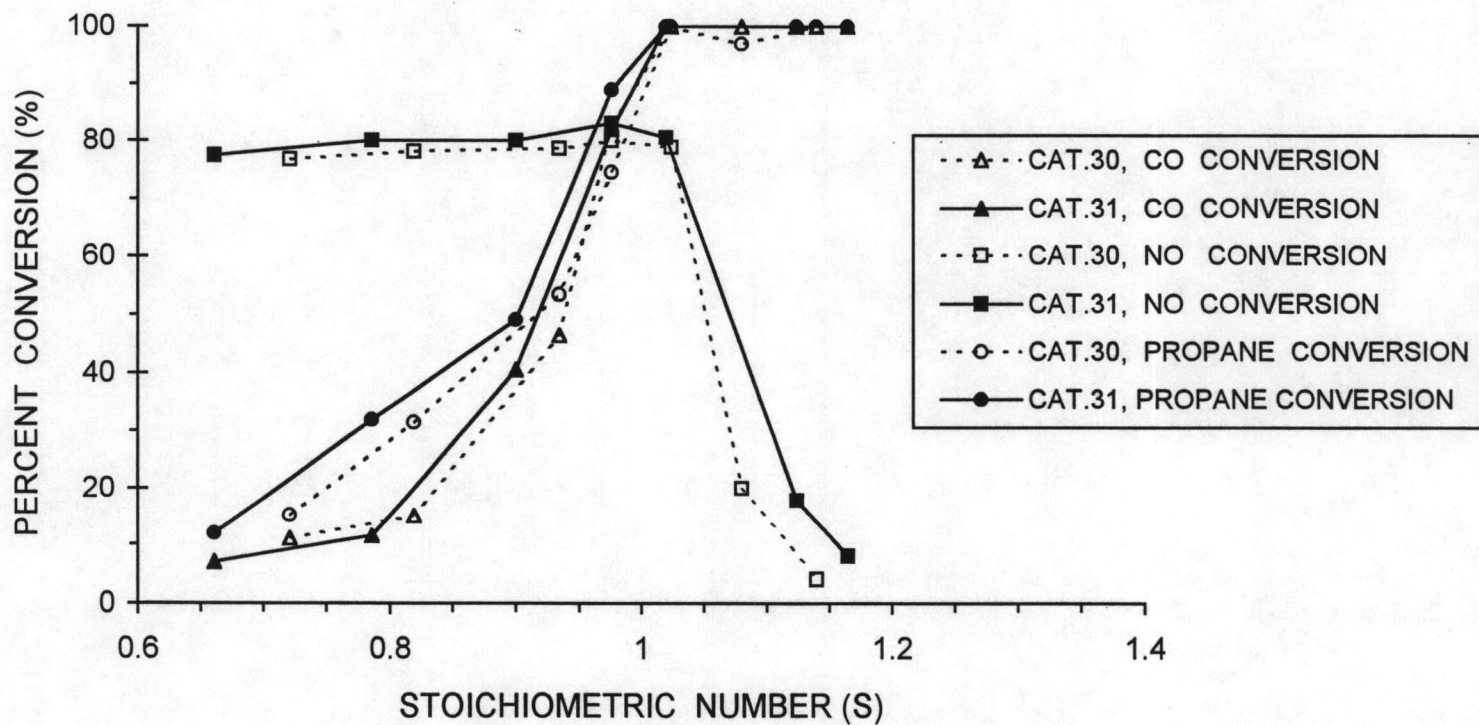


Figure 5.28 Effect of Air/Fuel Ratio on CAT.30 and CAT.31 for NO, CO and Propane Conversion of at 500 °C, GHSV = 15,000 h<sup>-1</sup>

The last purpose of this research is to compare the catalytic activity in term of Turnover Number (TON) between Pt support on alumina (CAT.27) and on washcoat monolith (CAT.31) catalyst. Both catalysts were pretreated in a simulated exhaust gas at the same condition,  $S_1=0.8$  at 300 °C for 2 hr. Hereby, the definition of TON is %NO converted to  $N_2$  conversion per molecule of active sites as illustrated in Figure 5.29. Figure 5.29 shows that TON of both catalysts increased at 300 °C. The maximum TON was observed at 500 °C and stay there after the reaction temperature was further increased.

It is observed that below 450 °C TON of both catalysts are nearly the same ; CAT.27 's is slightly higher than CAT.31 's. On the contrary, above 450 °C TON of CAT.27 's is obviously lower than CAT.31 's. It can be concluded that when the exhaust gas is hot, the chemical reaction rates are fast, and the overall conversion is controlled by pore diffusion and/or bulk mass transfer [20]. The active site and BET surface area are shown in Table 5.16 below.

Table 5.16 The active site and BET surface area of Pt catalyst supported on alumina and washcoat monolithic catalysts.

Catalyst	Active site (CO molecule/g.cat.)	BET (m <sup>2</sup> /g.cat)
CAT. 27	$2.83 \times 10^{17}$	250.791
CAT. 31	$3.01 \times 10^{17}$	146.760



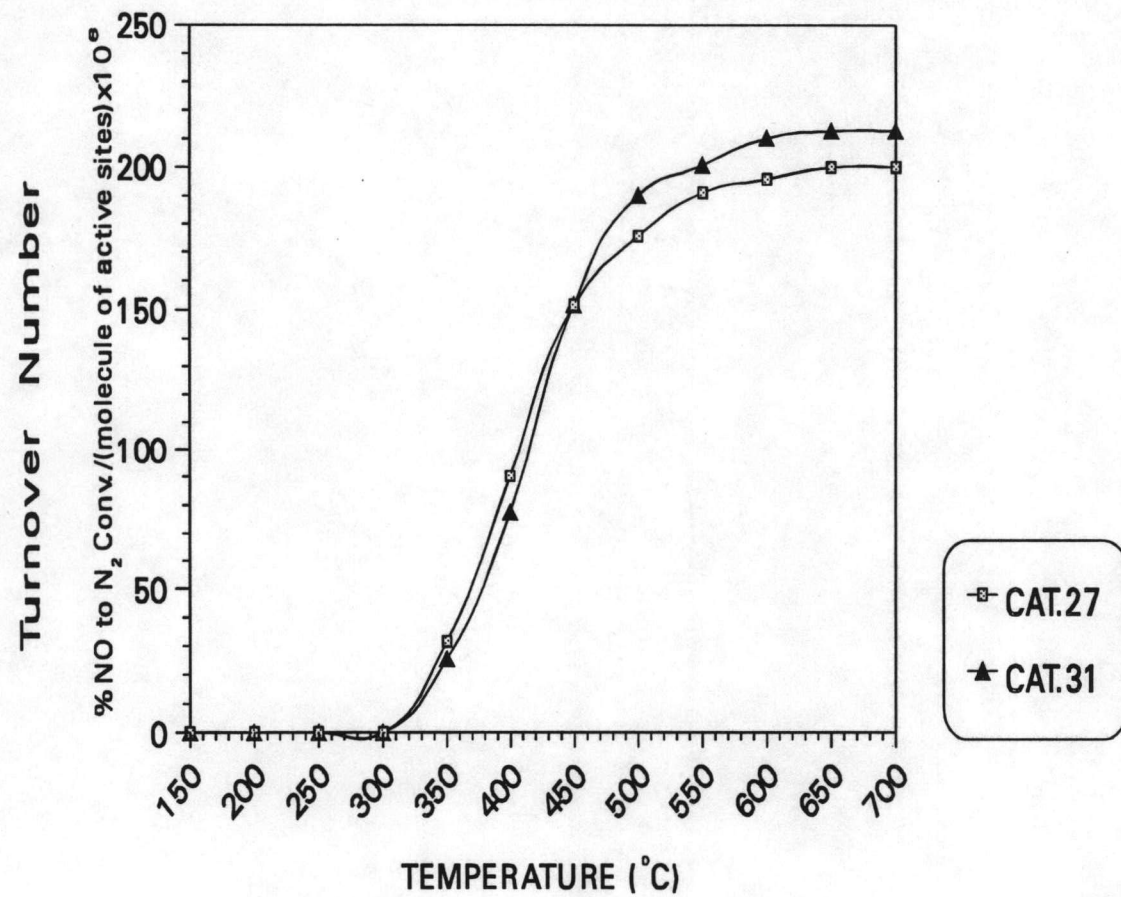


Figure 5.29 Turnover Number (TON) of Pt supported on alumina (CAT.27) and on washcoat monolithic (CAT.31) catalysts.