



## Chapter V

### Results and Discussions

Advanced automotive emission control technology coupled with sophisticated vehicle emission systems will be critical in helping to improve global air quality. Three-way catalysts based on rhodium, platinum and/or palladium formulations are nowadays state of arts technologies to substantially eliminate carbon monoxide, hydrocarbons and nitrogen oxides from the exhaust gas. The desired oxidation and reduction reaction proceed with high conversion rates in a closed loop catalyst arrangement when the exhaust gas composition equals a stoichiometric composition and when the catalyst achieves its normal operating temperature at appropriate space velocity.

In this research, the three-way catalysts were investigated for automotive exhaust gas emission removal. All of the reactions were fixed at stoichiometric composition in a fixed bed reactor. The results and discussions were categorized into three parts as follows :

5.1 The catalyst composition : In this part, the three-way catalyst formulations were carried out by;

- varying percent cerium loading,
- varying ratio of Pt-to-Rh,
- varying the order of loading of catalyst.

5.2 In this part, the effect of calcination temperature was studied on the activity of catalyst from section 5.1. The relationship between SMSI state and calcination temperature was investigated and discussed in detail.

5.3 Durability testing and investigation of the effect of A/F ratio ; Characterization and aging of some of catalysts were done. In this section the comparison of the aging and window between catalysts from section 5.1 and 5.2 were made. The window of catalysts was found to affect the efficiency of catalyst.

5.4 Development of the catalyst : The variation of preparation of catalyst from 5.2 were made to search for the improvement of catalyst performance. Using the pretreatment of fresh catalyst the catalytic performance could be developed. The details and results were discussed in this part.

## 5.1 The composition of catalysts.

### 5.1.1 Effect of Cerium Loading

The addition of cerium can promote the reactivity of automotive emission control catalysts. Its benefits can enhance both oxidation reaction of CO and HC and reduction reaction of  $\text{NO}_x$ . Cerium is one of the most important promoters [32]. Cerium significantly enhances  $\text{NO}_x$ , CO, and HC performance near stoichiometric air/fuel (A/F) ratios, acts as "Oxygen storage", improves resistance to thermal loss of BET surface area of the alumina support, stabilizes the active precious metals in a finely dispersed

state, and also enhances the water gas shift reaction for the removal of CO under  $O_2$ -deficient conditions [34].

From table 5.1, six catalysts, namely CAT.1 to CAT.6, were studied. This part is the effect of cerium addition on catalytic performance study. In this section, the variation of weight percent of cerium loading was done in the range of 0% to 13% while the ratio of Pt/Rh was fixed at 3:1. The catalytic performances were tested using (i) CO and HC oxidation reaction, and (ii)  $NO_x$  reduction reaction. After the activity test, all catalysts were characterized by using metal active sites and BET surface area measurement techniques.

Table 5.1 Prepared catalysts in this section.

Catalyst Sample	Metal Content
CAT. 1	0%Ce-0.01%Rh-0.03%Pt
CAT. 2	2%Ce-0.01%Rh-0.03%Pt
CAT. 3	5%Ce-0.01%Rh-0.03%Pt
CAT. 4	7%Ce-0.01%Rh-0.03%Pt
CAT. 5	9%Ce-0.01%Rh-0.03%Pt
CAT. 6	13%Ce-0.01%Rh-0.03%Pt

Figures 5.1, 5.2, and 5.3 show the conversion of CO, HC and NO as a function of reaction temperature. It was observed that the activity of catalyst increased as a function of the temperature. The more weight percent of cerium loaded, the more activities of the catalyst were.

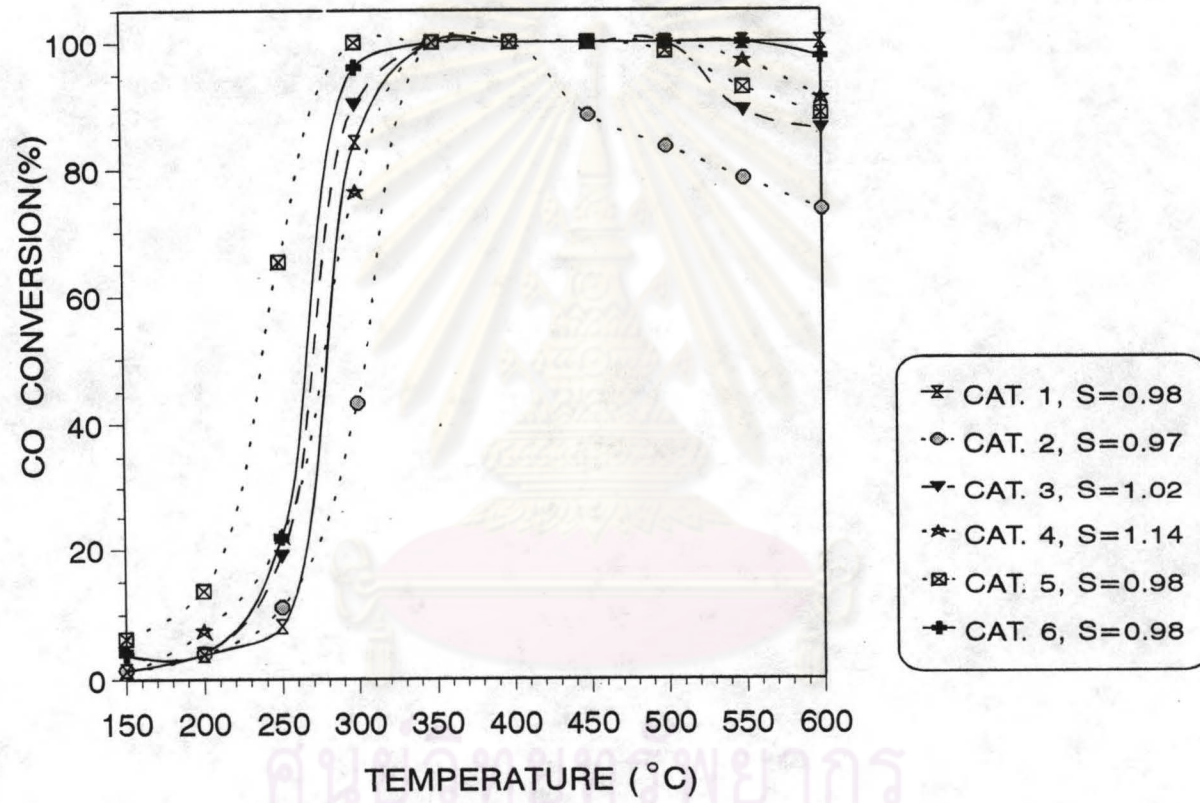


Figure 5.1 Temperature Dependence of CO Conversion on various percentages of cerium of three-way Catalysts.  
Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

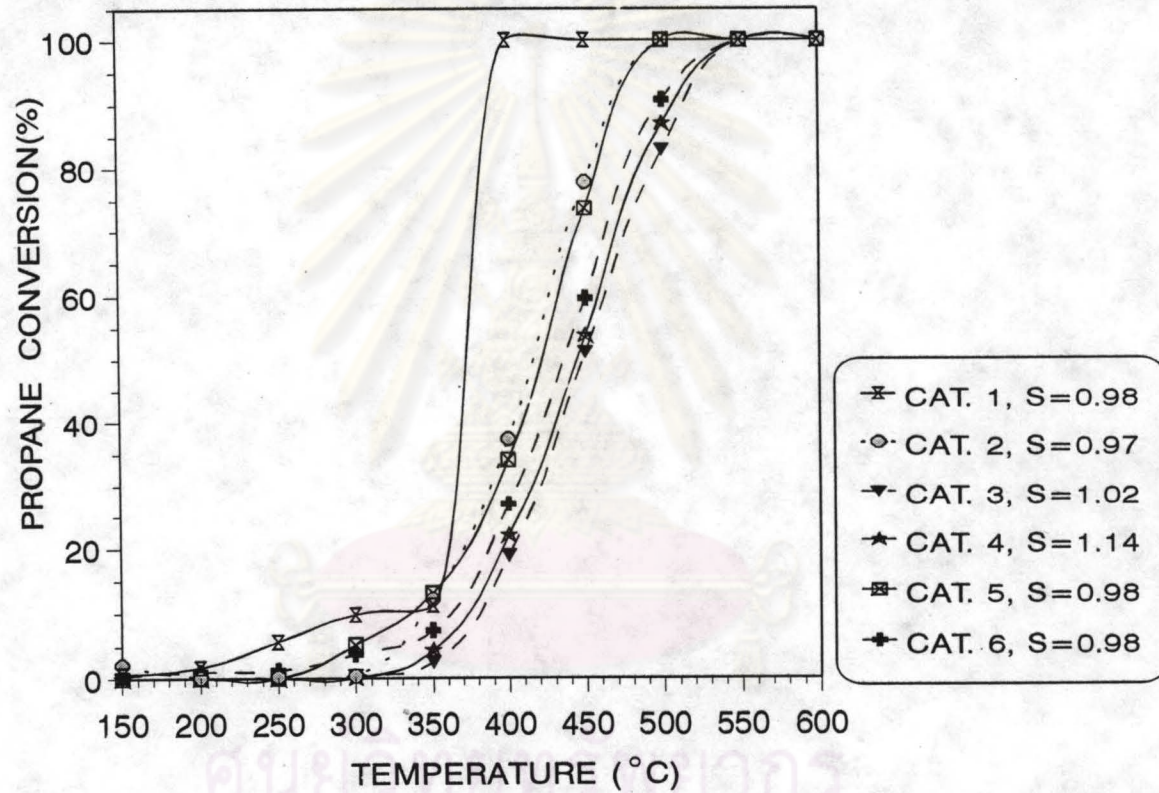


Figure 5.2 Temperature Dependence of Propane Conversion on various percentages of cerium of three-way Catalysts.

Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

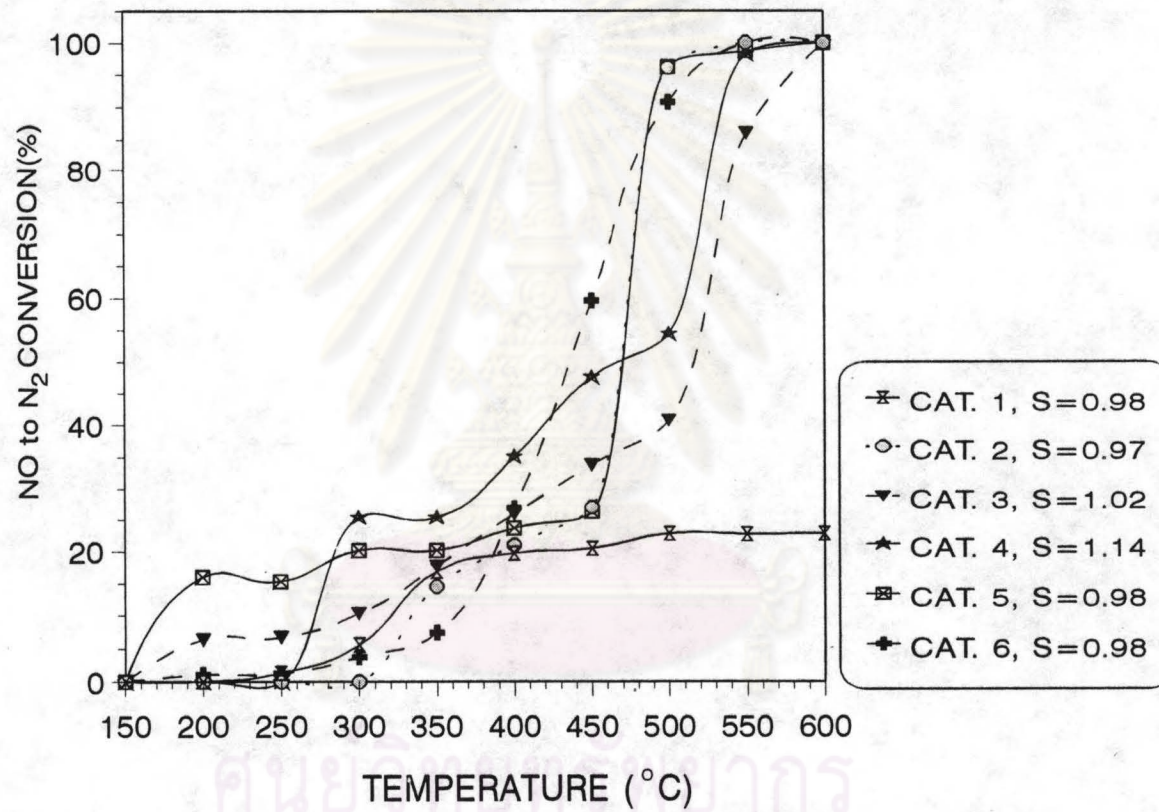


Figure 5.3 Temperature Dependence of NO Conversion on various percentages of cerium of three-way Catalysts.

Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

The results in Fig.5.1, 5.2 CAT.1 gave the high conversion of CO and HC. But in Fig.5.3, the results of NO to N<sub>2</sub> conversion of the catalyst with cerium and without cerium were absolutely different. In the case of CAT. 1 (without cerium), NO to N<sub>2</sub> conversion increased slightly with reaction temperature and reached a constant value at about 20%. Thus, it may be concluded that the addition of cerium can enhance the NO to N<sub>2</sub> conversion. Moreover, the variation of cerium content can promote the catalytic activity. From figure 5.1, the experimental curves can be divided into 2 ranges as follow : 150-400 °C and 400-600 °C. At low temperature (150-400 °C) CO conversion increased when the cerium content increased. CAT. 5 and CAT. 6 reached 100% conversion at 300 °C, while CAT. 2, CAT. 3, and CAT. 4 attained 100% at 350 °C. During the temperature range of 450-600 °C, CO conversion curves of catalysts with Ce decreased obviously. Especially, the CO conversion of CAT. 2 decreased to 75% at 600 °C, whereas increasing cerium content improved CO conversion and retarded the decrease at high temperature. The improvements increased consequently until the cerium content reached 13wt% and CO conversion attained 98% at 600 °C. While, CO conversion of CAT. 4 and 5 decreased more than that of CAT. 6, CAT. 4 and 5 exhibited the CO conversion much higher than those of CAT. 2 and 3. The CO conversion of CAT. 5 attained 94% at 600 °C.

The decrease of CO conversion at high temperature range was affected by Ce addition. Yao and Yao [19] reported that the capacity of oxygen storage increased more in high temperature than low temperature. While the cerium content increased, the capacity of oxygen storage was kept constant.

For propane conversion (Fig. 5.2), the addition of cerium can enhance the activity too, though the increase of weight percent of cerium loading (CAT. 2-CAT. 6) did little for the improvement of the activity. Thus, the high performance of the prepared catalyst for propane conversion cannot be much improved by cerium addition [29].

When NO to N<sub>2</sub> conversion was considered, the effect of Ce addition was shown by the obvious result that the maximum conversion of CAT. 1 without Ce was 20% while the addition of only 2wt% of cerium can improve the NO to N<sub>2</sub> conversion, as well as lead to 100 % at 550°C. Similarly, CAT. 3 and CAT. 4 (with 5 and 7%wt cerium) can increase the oxygen storage capacity at high temperature; NO conversion of CAT. 3 and 4 can rise up to 100% at 600 °C. Furthermore, the increase of Ce content up to 9 wt% not only increased the NO conversion but also reduced all NO at lower temperature. However, if the Ce content is more than 9 wt% the catalytic activity will be not improved. Clearly, the addition of 9wt%Ce (CAT. 5) showed the highest conversion at 500 °C. But, the addition of 13 wt%Ce (CAT. 6) gave the reverse result of NO to N<sub>2</sub> conversion which was about only 17% at 500 °C.

Table 5.2 summarizes the light-off temperature, the temperature that showed the 50% conversion, for the oxidation of CO and propane and the reduction of nitric oxide on various catalysts. CAT. 5 exhibited the highest activity on all kinds of reaction. From table 5.2 one can see that CAT. 5 showed the highest overall activity on all of the reactions. This conclusion comes from the shift to lower light-off temperatures of this catalyst. This shift is possibly the result of Ce.



Table 5.2 The light - off temperature of the prepared catalysts.

Catalyst	Light - off Temperature (°C)		
	CO	C <sub>3</sub> H <sub>8</sub>	NO
CAT. 1	278	375	-
CAT. 2	302	422	470
CAT. 3	270	442	511
CAT. 4	277	440	508
CAT. 5	240	424	470
CAT. 6	262	442	570

Table 5.3 showed the amount of catalyst active sites which was measured by CO chemisorption and BET surface area. As the physical properties data of alumina shown in Appendix B, surface area of alumina was about 350 m<sup>2</sup>/g but BET surface area of the catalysts shown in table 5.3 was in the range from 147 to 190 m<sup>2</sup>/g. This result could be explained that the pores of support was plugged by the loaded metal (Pt, Rh, and Ce). Therefore, the surface area of catalyst was lower than the surface area of alumina.

Table 5.3 The active site and BET Surface Area of prepared catalysts

Catalyst	Active Site (molecule/g, cat.)	BET Surface Area (m <sup>2</sup> /g. cat.)
CAT. 1	2.36X10 <sup>18</sup>	167.29
CAT. 2	2.43X10 <sup>18</sup>	147.89
CAT. 3	1.21X10 <sup>18</sup>	126.89
CAT. 4	2.82X10 <sup>18</sup>	154.45
CAT. 5	1.78X10 <sup>18</sup>	186.75
CAT. 6	1.22X10 <sup>18</sup>	194.45

From the previous results, it can be suggested that, there is a promotional effect of Ce addition. Its role in three-way catalysts (TWC) had been variously described as: oxygen storage component under the cyclic lean-rich composition. This fluctuation is common when the automotive engine is operated at near the stoichiometric point. The CeO<sub>2</sub> component provides oxygen, which is stored under lean conditions, for the CO oxidation activity, it may lead to the higher performance for HC and NO<sub>x</sub> conversion [32].

### 5.1.2 Effect of Pt/Rh ratio on Catalytic Performance

Table 5.4 shows all the catalysts prepared by varying the ratio of Pt/Rh.

Table 5.4 Variation of Pt/Rh ratio of catalysts

Catalyst Sample	Metal Content (wt%)
CAT. 7 (9%Ce ; 2:1)	9%Ce-0.015%Rh-0.03%Pt
CAT. 5 (9%Ce ; 3:1)	9%Ce-0.01%Rh-0.03%Pt
CAT. 8 (9%Ce ; 4.3:1)	9%Ce-0.007%Rh-0.03%Pt
CAT. 9 (9%Ce ; 6:1)	9%Ce-0.005%Rh-0.03%Pt
CAT. 10 (9%Ce ; 8:1)	9%Ce-0.00375%Rh-0.03%Pt

The temperature dependence of CO, C<sub>3</sub>H<sub>8</sub>, and NO to N<sub>2</sub> conversion on prepared catalysts, are shown in figures 5.4, 5.5, and 5.6, respectively.

The CO conversion of prepared catalysts, depends on the temperature of reaction and the ratio of Pt/Rh studied catalysts. Figure 5.4 shows the CAT. 7 and CAT. 5 having the decreasing conversion in the temperature range of 500-600 °C during CAT. 8, CAT 9, and CAT. 10 obtained the higher conversion.

The effect of Rh content on the C<sub>3</sub>H<sub>8</sub> conversion shown in Fig. 5.5 is similar to the activity of CO conversion shown in Fig. 5.4. The

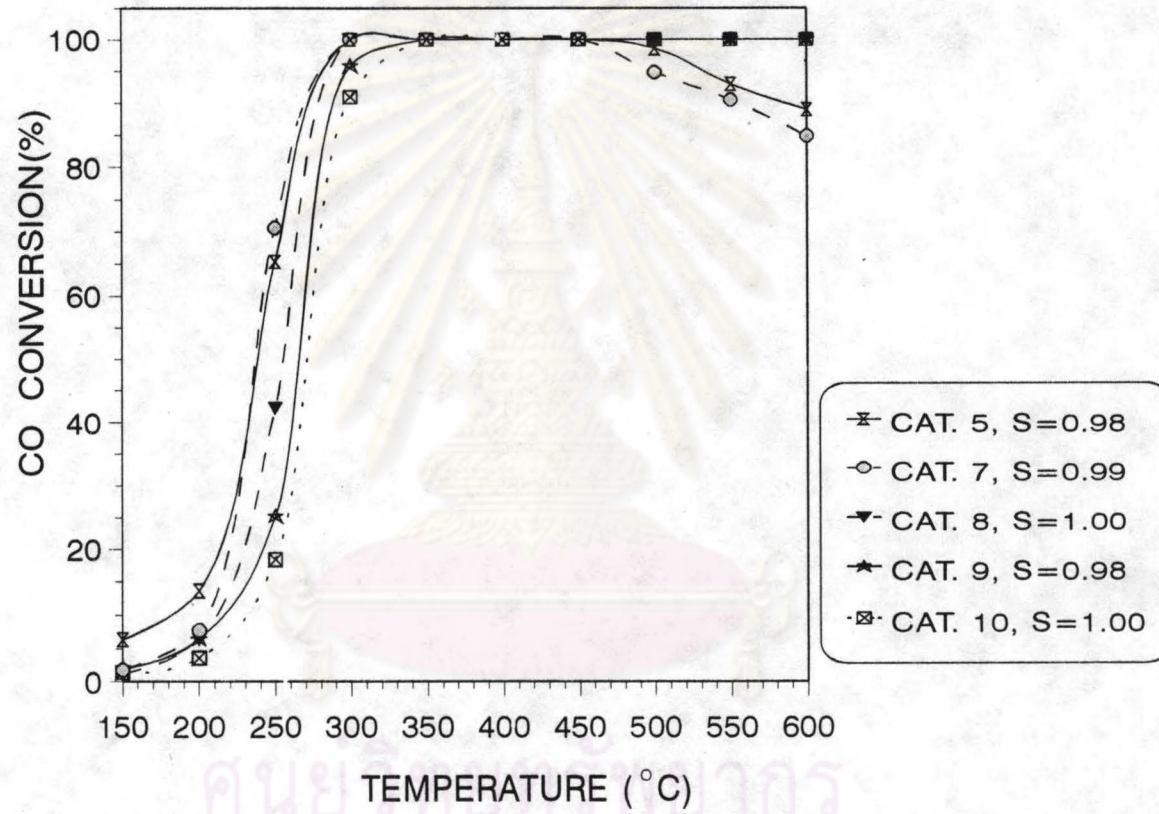


Figure 5.4 Effect of Pt/Rh ratio for CO Conversion on three-way catalysts.

Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

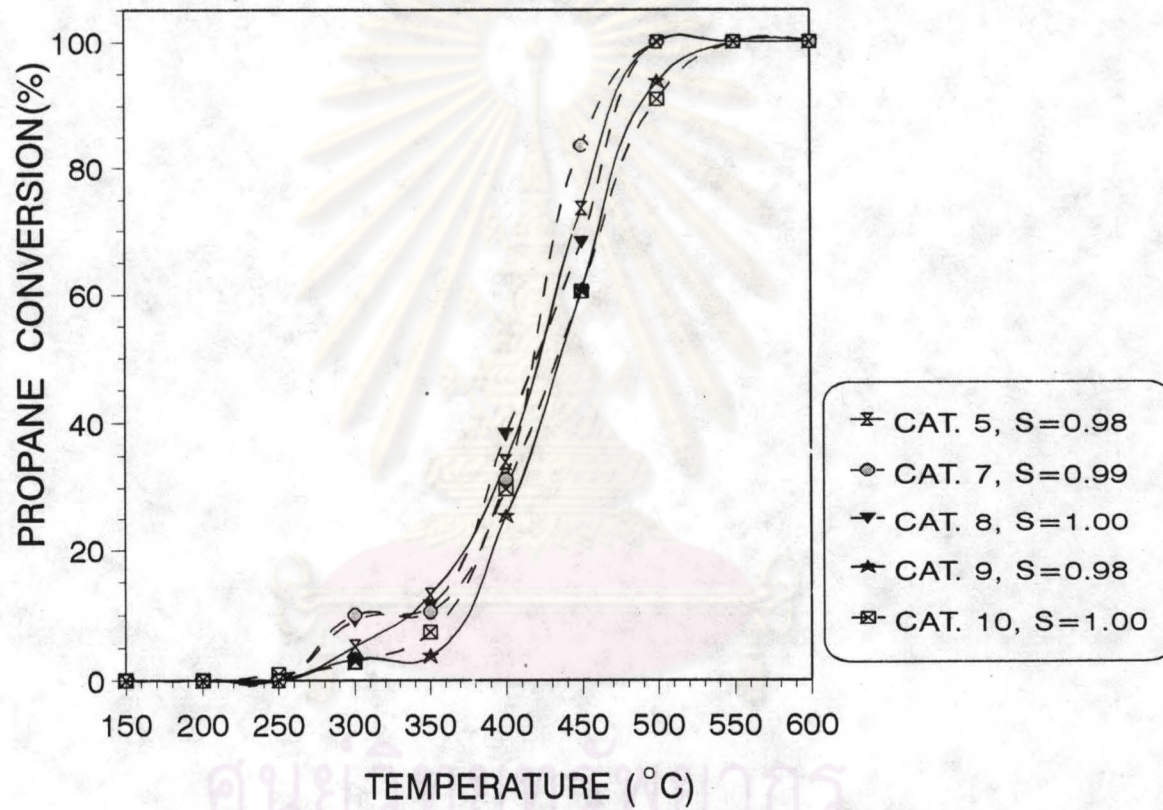


Figure 5.5 Effect of Pt/Rh ratio for Propane Conversion on three-way catalysts. Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

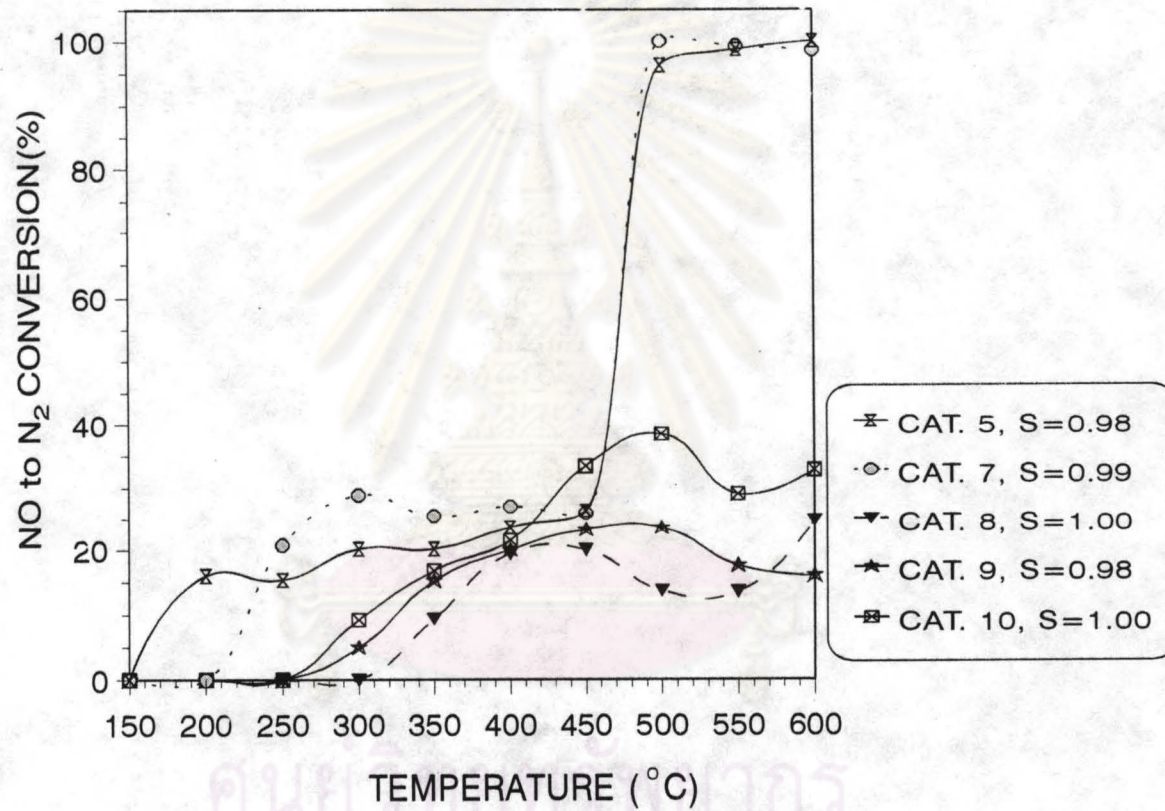


Figure 5.6 Effect of Pt/Rh ratio for NO Conversion on three-way catalysts.  
Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

lowest ratio of catalyst exhibited the maximum activity at 550 °C. The activities of CAT. 7 and CAT. 5 were higher than CAT. 8, 9, and 10. The propane conversion on CAT. 7 and 5 attained 100% at 500 °C while CAT. 8, 9, and 10 gave 100% propane conversion at 550 °C.

The experimental results observed during NO to N<sub>2</sub> reduction were significantly different from those observed during CO or C<sub>3</sub>H<sub>8</sub> oxidation. On the contrary, the activities of catalysts on NO conversion were decreased as soon as the ratio of catalysts were increased. Fig. 5.6 clearly shows that the variation of Rh content slightly affected NO to N<sub>2</sub> conversion. However, when the Rh content was increased from 0.007% to 0.01%, NO conversion could jump from around 30% to 100% at high temperatures.

The light-off temperature of the prepared catalysts are shown in Table 5.5. Since NO conversions of CAT. 8, 9, and CAT. 10 were always lower than 50%, therefore, these 3 catalysts had no light-off temperature for NO. The activities of CAT. 7 and CAT. 5 were slightly different on propane and NO conversion. From these results, one can conclude that the best catalysts were CAT. 7 and CAT. 5.

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Table 5.5 The light - off temperature of the prepared catalysts.

Catalyst	Light - off Temperature (°C)		
	CO	C <sub>3</sub> H <sub>8</sub>	NO
CAT. 5	240	424	470
CAT. 7	235	417	473
CAT. 8	260	417	-
CAT. 9	270	440	-
CAT. 10	273	435	-

It was suggested as mentioned above that the increment of Rh content can give the positive and negative effect on the catalytic activity. The high amount of Rh content can enhance the activity of CO at temperature range of 150-300 °C, the ability of C<sub>3</sub>H<sub>8</sub> oxidation at high temperature region. At the same time, the high Rh content can improve the NO conversion, especially, at temperature range 450-600 °C. Although the CO conversion at high temperature region of high Rh content catalyst decrease.

From the descriptions of experimental data, the CO conversion of these catalysts for CO oxidation reaction was affected by the increment of Rh content. The increment of Rh could get the supported rhodium-platinum alloy. The supported rhodium-platinum alloy catalyst tended to become Rh-enriched by migration of the rhodium component in the alloy surface [20]. While at a high ratio of Pt/Rh, Pt played an important role in the oxidation of CO [28]. While at low ratio ratio of Pt/Rh, high Rh content on  $\gamma$ -alumina support could promote the oxidation of C<sub>3</sub>H<sub>8</sub> [33]. Furthermore at the low ratio of Pt/Rh, the activity of the reduction reaction of NO was more active due to high Rh content.



The measured active sites and BET surface areas are tabulated in Table 5.6 below.

Table 5.6 The active sites and BET surface area of prepared catalysts

Catalyst	Active Site (molecule/g, cat.)	BET Surface Area (m <sup>2</sup> /g. cat.)
CAT. 5	1.78X10 <sup>18</sup>	186.75
CAT. 7	1.61X10 <sup>18</sup>	213.03
CAT. 8	2.037X10 <sup>18</sup>	183.48
CAT. 9	1.962X10 <sup>18</sup>	196.77
CAT. 10	1.113X10 <sup>18</sup>	137.65

The active sites measurement could support the platinum-rhodium alloy model. From CAT. 10 to CAT. 8, the Rh content increased, as the value of active site increased. But at the low Pt/Rh ratio, the high Rh content might give an alloy effect resulting in obvious decrease of, the value of active site. Rh-migration could affect the active sites of Pt which converted the CO pollutant. Thus, CO conversion was decreased at high temperature.

For these reasons, the orders of activity of all the reactions were

CO conversion :

CAT. 10 ~ CAT. 9 ~ CAT. 8 > CAT. 5 > CAT. 7

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

CAT. 7 ~ CAT. 5 > CAT. 8 > CAT. 9 > CAT 10

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

CAT. 7 ~ CAT. 5 >> CAT. 10 > CAT. 9 > CAT. 8

Therefore, the catalyst with the best overall performance was 9wt%Ce-0.01%Rh-0.03%Pt (CAT. 5).



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### 5.1.3 Effect of Loading Order of Catalyst on Catalytic Performance

The results from the two sections above indicated that the most suitable catalyst was 9 wt%Ce - 0.01 wt%Rh - 0.03 wt%Pt (CAT. 5). In this section, this catalyst was prepared by various methods. The selected methods were :

1. Cerium, rhodium, and platinum were coimpregnated on the support. (Coimpregnated) (CAT. 11)

2. Cerium was impregnated first before being calcined. Then platinum was impregnated following the calcination. Finally, the sample was impregnated with rhodium and calcined. (Ce - Pt - Rh) (CAT. 12)

3. Cerium was impregnated first before being calcined. Then rhodium was impregnated following the calcination. Finally, the sample was impregnated with platinum and calcined. (Ce - Rh - Pt) (CAT. 5)

The effect of temperature on the conversion of CO to CO<sub>2</sub>, propane to CO<sub>2</sub> and H<sub>2</sub>O and NO to N<sub>2</sub> conversion by protonated coimpregnate, Ce - Pt - Rh, and Ce - Rh - Pt are shown in figures 5.7-5.9 and table 5.7, respectively. The result in Fig 5.7, can be divided into 3 ranges as follows : 150 - 300 °C, 300-450 °C, and 450 - 600 °C. During the low temperature range when the reaction temperature was raised the activity of CAT. 11 rised faster than the other two. But finally all the catalyst activities gave the maximum value (100%) all together at 300 °C. However the increasing rates of the 3 catalysts were not significantly different.

During the middle temperature range all the catalysts show equivalent activity (ie.100%). But when the reaction temperature reached the

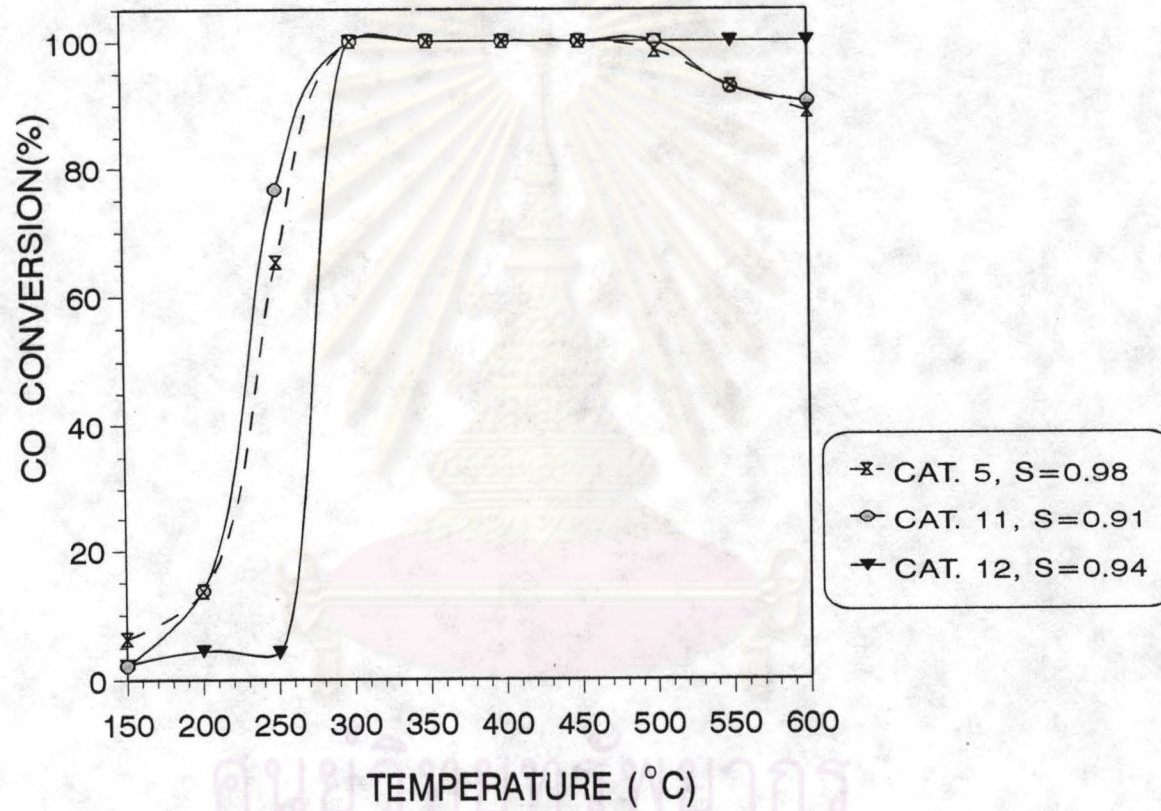


Figure 5.7 Temperature Dependence of CO Conversion on various loading sequential of three-way catalysts.

Stoichiometric number = 1, GHSV = 15,000.h<sup>-1</sup>.

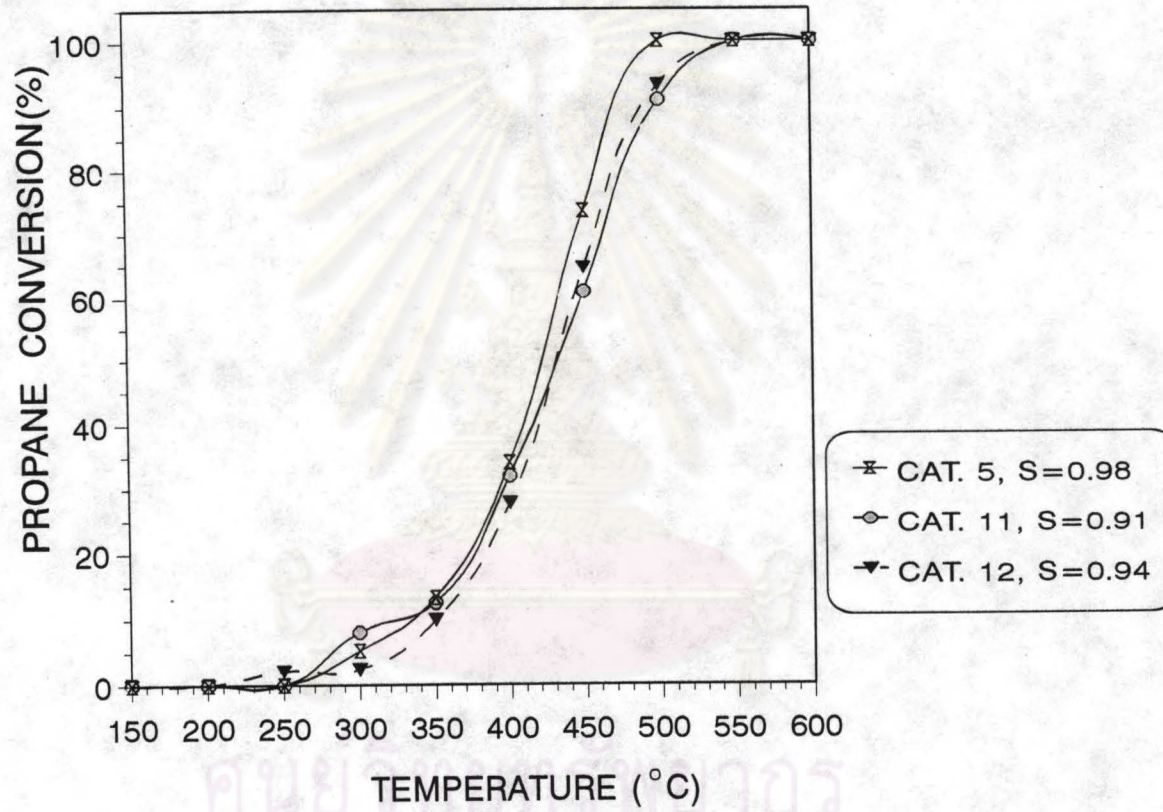


Figure 5.8 Temperature Dependence of Propane Conversion on various loading sequential of three-way catalysts. Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

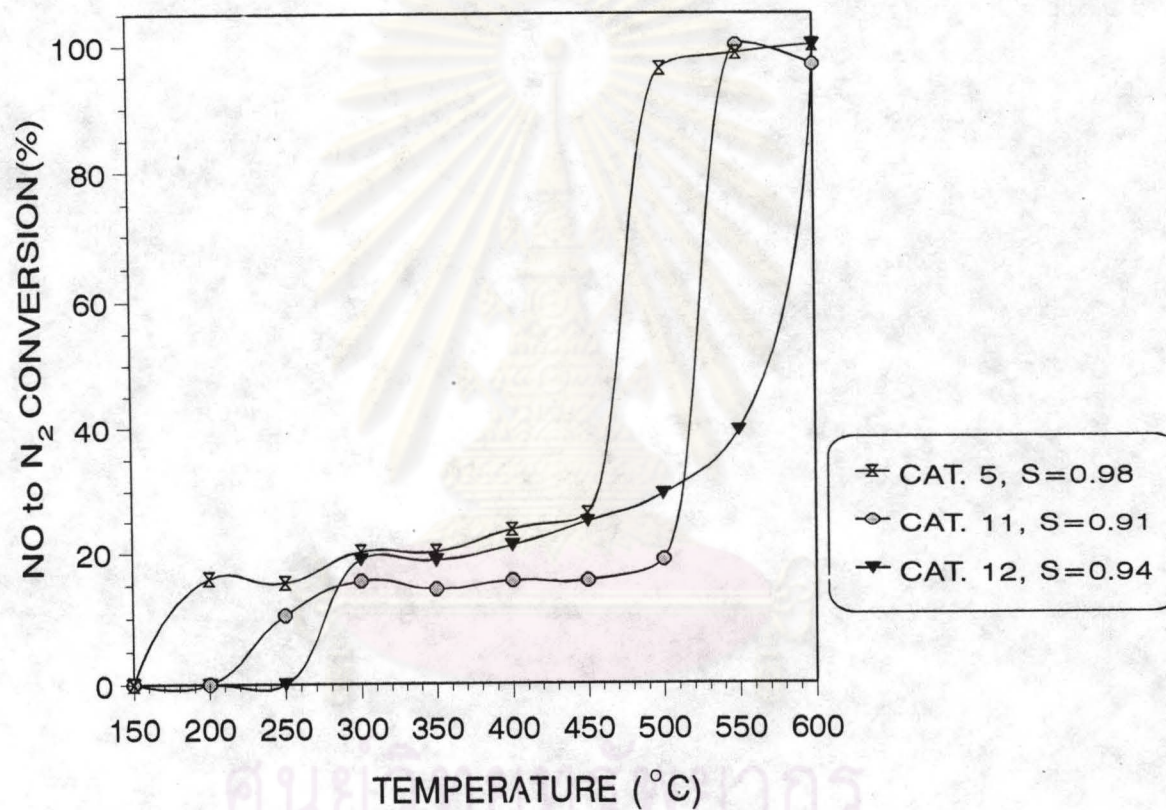


Figure 5.9 Temperature Dependence of NO Conversion on various loading sequential of three-way catalysts.

Stoichiometric number = 1, GHSV = 15,000 h<sup>-1</sup>.

high temperature region, the catalyst activities became different again. CAT. 11 was the only one which could maintain the CO conversion at 100% while the conversions of the other two slightly dropped to about 90%.

From figure 5.8, one can see that all 3 catalysts had similar propane conversion reaction temperature curves. The only difference was that the activity of CAT. 5 reached the maximum value slightly before the rest.

The loading order had obvious effects when considering NO reduction reaction was considered. Figure 5.9 shows that at a temperature below 400 °C, the catalytic activities of all the catalysts were not significantly different. However, when the reaction temperature was increased beyond 400 °C the NO conversion of CAT. 5 rapidly jumped to 100% at a temperature about 470 °C. The NO conversion of CAT. 11 reached 100% at a temperature about 550 °C which was 80 °C higher than that of CAT. 5. CAT. 12 showed the worst performance. Since it could convert only 30% of NO at 550 °C. However, its NO conversion could reach 100% after the reaction temperature was increased to 600 °C.

The light-off temperatures, the temperatures that show 50% conversion, are presented in table 5.7. The light-off temperature of various catalysts depended on the loading order of catalyst. It was thus concluded that Ce-Rh-Pt (CAT. 5) was the most effective catalyst for the removal of three pollutants in exhaust gas.

Table 5.7 The light - off temperatures of the various catalysts.

Catalyst	Light - off Temperature (°C)		
	CO	C <sub>3</sub> H <sub>8</sub>	NO
CAT. 5	240	424	470
CAT. 11	240	427	575
CAT. 12	252	427	520

The active site and BET surface area of the catalysts in this part are illustrated in table 5. 8. The order of active sites was

$$\text{CAT. 5} > \text{CAT. 12} > \text{CAT. 11}$$

Table 5.8 The active site and BET surface of all catalysts

Catalyst	Active Site (molecule/g, cat.)	BET Surface Area (m <sup>2</sup> /g. cat.)
CAT. 5	1.78X10 <sup>18</sup>	186.75
CAT. 11	0.91X10 <sup>18</sup>	133.43
CAT. 12	1.29X10 <sup>18</sup>	179.00

The result of active site measurement could confirm the activity of catalyst as mentioned above.

The results described above agreed with those previously reported by Marecot et al [36, 37] and Hegedus et al [47]. Marecot et al demonstrated that the catalytic activity of catalyst prepared by sequential impregnation was higher than the activities of the catalyst prepared by coimpregnation. While



Hegedus et al concluded that a layer catalyst having an exterior layer principally platinum and an interior layer with the major portion of the rhodium on the catalyst, resulted in improved overall three-way performance when operated close to the stoichiometric point.



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## 5.2 Effect of the Calcination Condition on Catalytic Performance.

This part of experiment was designed to study the modification of the conventional three-way catalyst. The objective of the modification is to develop a high performance three-way catalyst. The modification was performed by changing the atmosphere and temperature of calcination of three conventional catalysts. The conventional catalyst was 9 wt%Ce-0.01 wt%Rh-0.03 wt%Pt (CAT. 5) calcined in a reference conditions (ie. in air at 500 °C). The modified calcination conditions are shown in Table 5.9.

Table 5.9 The prepared catalysts in this part.

Catalyst Sample	Calcination Condition
CAT. 5(conventional)	Calcined in air at 500° C (ref. condition)
CAT. 13	Calcined in 10%H <sub>2</sub> at 400° C
CAT. 14	Calcined in 10%H <sub>2</sub> at 500° C
CAT. 15	Calcined in 10%H <sub>2</sub> at 600° C
CAT. 16	Calcined in 10%H <sub>2</sub> at 700° C

The results of CO, C<sub>3</sub>H<sub>8</sub>, and NO to N<sub>2</sub> conversion at the temperature range of 150 - 600 ° C are shown in figures 5.10, 5.11, and 5.12, respectively.

The modified catalysts gave the interesting influence on the efficiency and CO conversion of catalyst. Figure 5.10 shows the advantage of calcination in a H<sub>2</sub> atmosphere for the oxidation of CO to CO<sub>2</sub>. The results clearly show that the catalysts calcined in the H<sub>2</sub> atmosphere were much

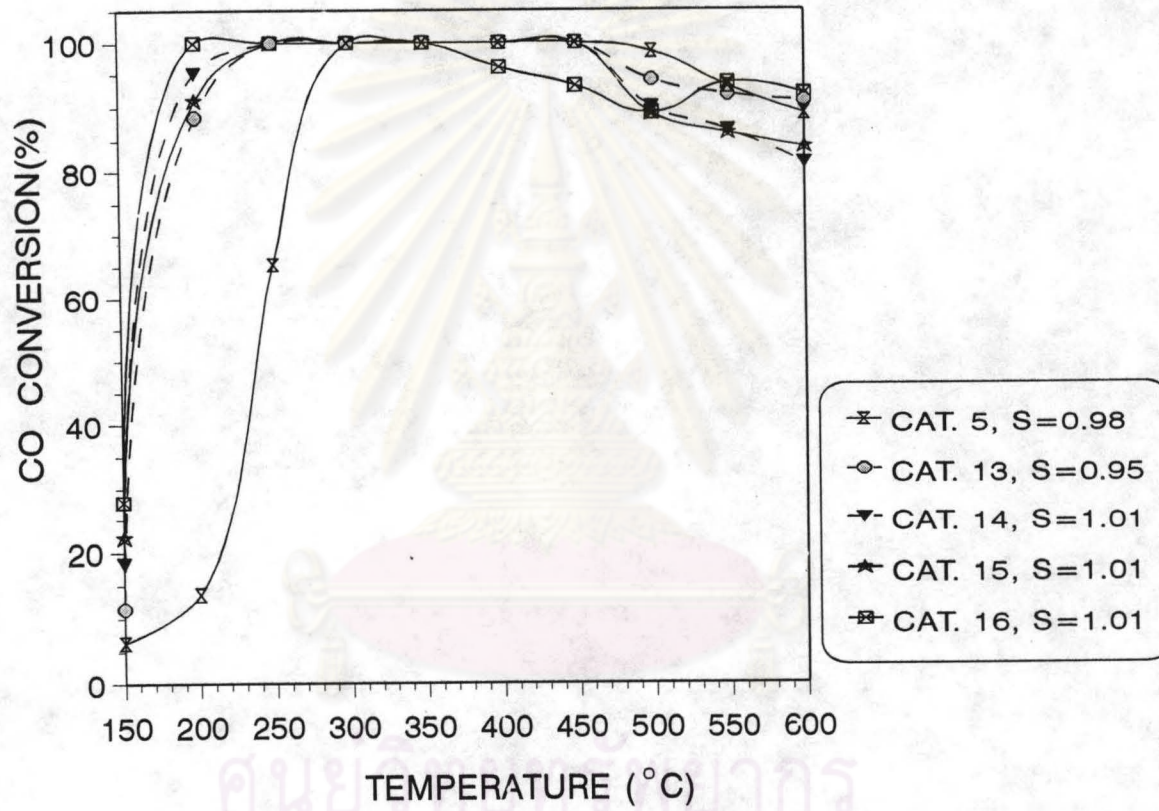


Figure 5.10 Temperature Dependence of CO Conversion on various calcination temperature in three-way catalysts. Stoichiometric number = 1, GHSV = 15,000<sup>-1</sup>.

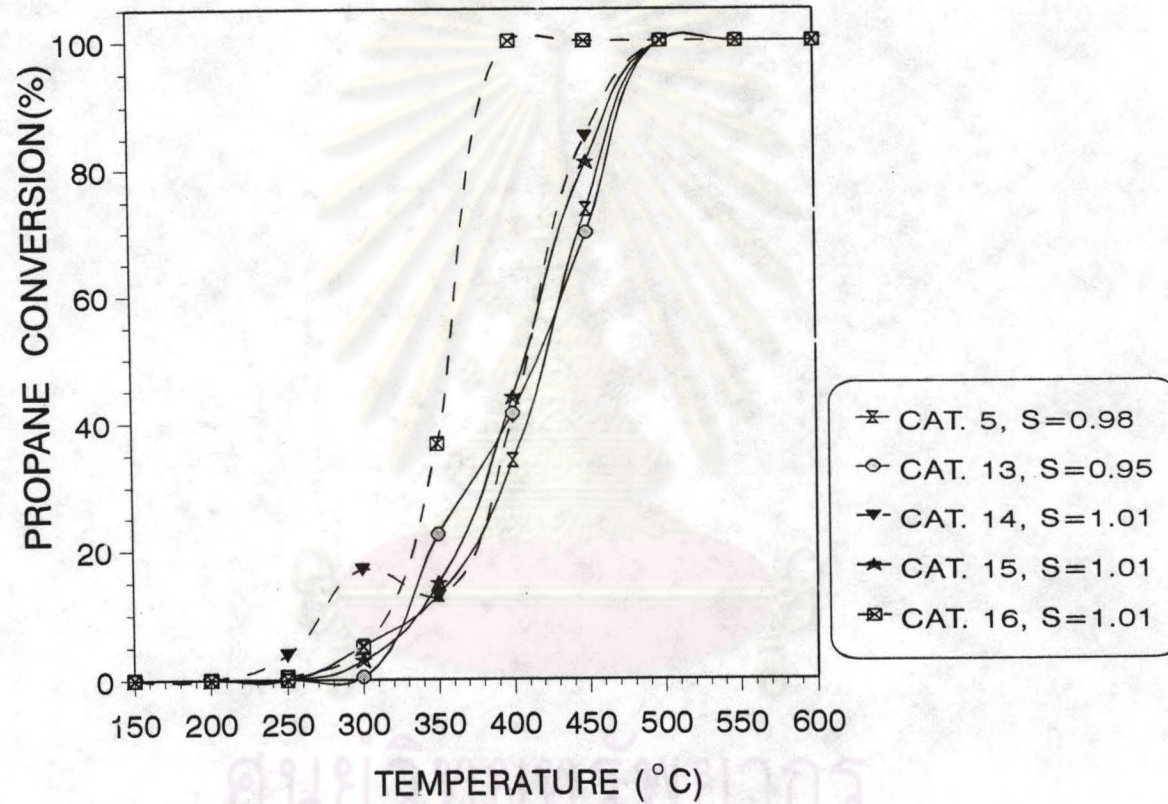


Figure 5.11 Temperature Dependence of Propane conversion on various calcination temperature in three-way catalysts. Stoichiometric number = 1, GHSV = 15,000<sup>-1</sup>.

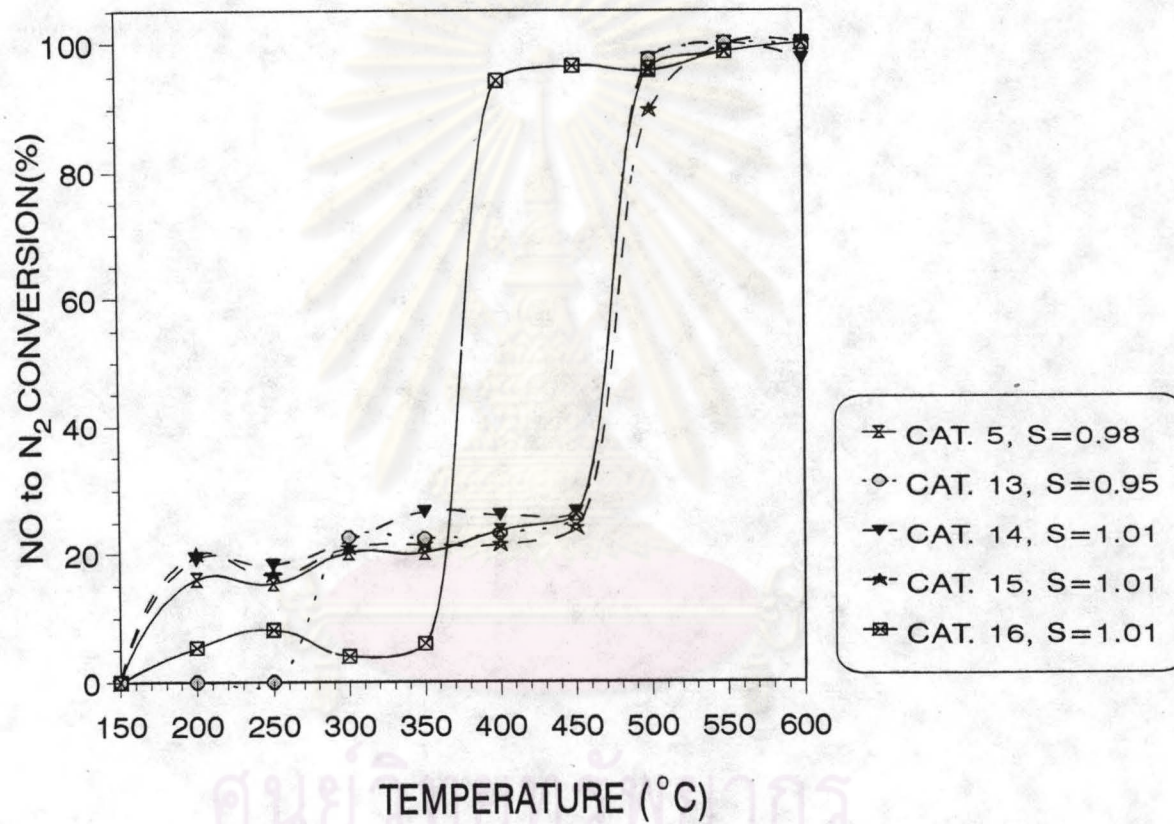


Figure 5.12 Temperature Dependence of NO Conversion on various calcination temperature in three-way catalysts. Stoichiometric number = 1, GHSV = 15,000<sup>-1</sup>.

more active than the conventional ones. While the calcination condition of the modified catalyst was reducing atmosphere ( $H_2$ ) at 400 °C [CAT. 13], the CO conversion attained 100% at only 250 °C. The variation of calcination temperature until 600 °C [CAT. 5] gave the maximum conversion (100%) at only 200 °C.

The modified catalysts gave similar results of  $C_3H_8$  conversion, as shown in figure 5.11 to  $CO_2$  conversion. The results indicated that calcination in the  $H_2$  atmosphere could improve the activity of the catalyst if the calcination temperature was higher than 500 °C. The catalyst calcined in  $H_2$  atmosphere between 400-500 °C (CAT. 13, 14) did not show any improvement over the conventional catalyst (CAT. 5). But when the calcination temperature was increased beyond 500 °C (eg. 600 °C) and 700 °C (CAT. 16) the improvement of the catalytic activity became evident.

Finally, the effect of the modification of conventional three - way catalyst on NO conversion was considered. From Figure 5.12, CAT. 13 and CAT. 14 exhibited their activities and efficiencies slightly different from conventional three - way catalyst. It was found that CAT. 13 and CAT. 14 showed higher catalytic activity than CAT. 5 during the temperature range of 150-450 °C and showed equal catalytic activity to CAT. 5 during the temperature range of 500-600 °C. Influence of calcination temperature on the decrease of temperature of maximum conversion was obviously observed on CAT. 15 and CAT. 16. The temperature of maximum NO conversion on CAT. 15 shifted down from about 500 °C to about 450 °C. And the temperature of maximum NO to  $N_2$  conversion on CAT. 16 was drastically shift down from 500 °C to 400 °C. It was thus concluded that CAT. 16 was



the strong candidate for NO reduction reaction. As shown in Table 5.10, the results of the light-off temperature of all the catalysts in this part indicated that CAT. 16 attained 50% conversion at the lowest temperature.

Table 5.10 The light - off temperatures of catalysts in this part.

Catalyst	Light - off Temperature (°C)		
	CO	Propane	NO
CAT. 5	240	424	470
CAT. 13	162	410	470
CAT. 14	160	407	470
CAT. 15	160	390	420
CAT. 16	155	351	375

From the results described above, it can be suggested that the catalytic activity depended on the calcination atmosphere. The calcination atmosphere can develop the efficiency and activity of catalysts. This phenomena may involve the strong metal support interaction effect (SMSI).

The evidence of strong - metal - support - interactions was suggested to be able to occur on the reduction of group VIII metals supported on reducible oxides at temperature in excess of 427 C [48]. The reduction at high temperature could suppress hydrogen carbon monoxide adsorption at room temperature. The more noble metals were more strongly affected. This effect can be verified by CO-adsorption measurement. From the results as shown in table 5.11, the amount of active site decreased as the calcination temperature was increased. Whereas the BET surface area got no effect from the calcination temperature.

Table 5.11 The BET surface area and Active site of catalysts prepared by different calcination atmosphere.

Catalyst	Active Site (CO molecule/g. cat.)	BET (m <sup>2</sup> /g. cat )
CAT. 5*	1.78X10 <sup>18</sup>	186.75
CAT. 13**	1.808X10 <sup>18</sup>	191.57
CAT. 14**	1.201X10 <sup>18</sup>	203.79
CAT. 15**	0.449X10 <sup>18</sup>	159.00
CAT. 16**	0.514X10 <sup>18</sup>	214.11

\* Atmosphere : Air 500 °C 4 hours

\*\* Atmosphere : 10% H<sub>2</sub>/N<sub>2</sub>

The active site measurement can give the particle size of metal. The decrease of CO showed that the metal particle size was increased by the reducing calcination atmosphere and high temperature calcination. These effect could be attributed to the strong-metal-support-interaction phenomenon.



### 5.3.1 Effect of Time on Stream on Catalytic Performance. (Durability Testing)

The relative durability performances of the conventional three - way catalyst and the modified catalyst were observed for 48 hours of operation under simulated automotive exhaust gas. Catalyst performances at 600 °C are shown in the figures 5.13, 5.14, and 5.15 as integral conversion about the stoichiometric point ( $S=1$ ). The figures show the results of testing of the catalysts being aged for 48 hours.

The results indicated that all the catalysts were not affected from aging. They could resist to sintering. Compared to conventional three-way catalyst, the modified catalyst had a higher CO conversion. The conventional three-way catalyst appeared to behave just like the modified catalyst for  $C_3H_8$  conversion which was constant at 100% throughout 48 hours. The best catalyst for NO conversion was the modified one. The NO to  $N_2$  conversion of the modified catalyst was slightly higher than the conventional three-way catalyst.

The comparative assessment of the results between the conventional three-way catalyst and the modified catalyst in Figure 5.16 indicated that there were slightly differences between two catalysts. After aging, both of them were still stable and gave the high efficiency.

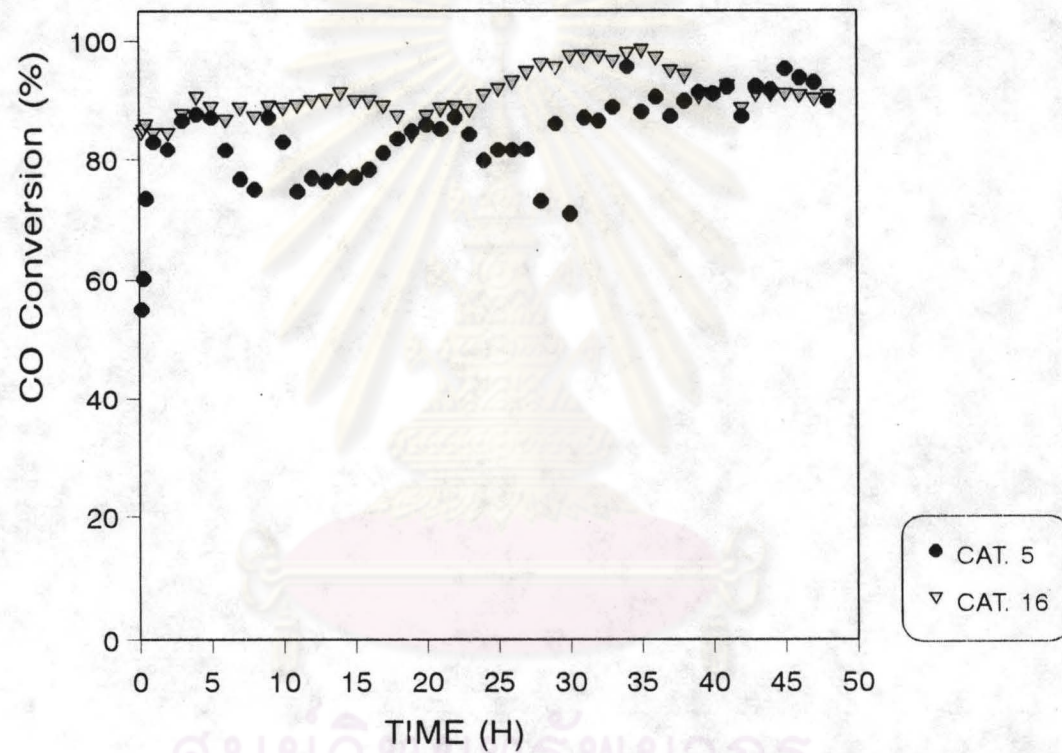


Figure 5.13 Effect of time on stream on CO conversion of CAT. 5 and CAT. 16. Condition aging 48 h. at 600 °C Stoichiometric Number = 1.

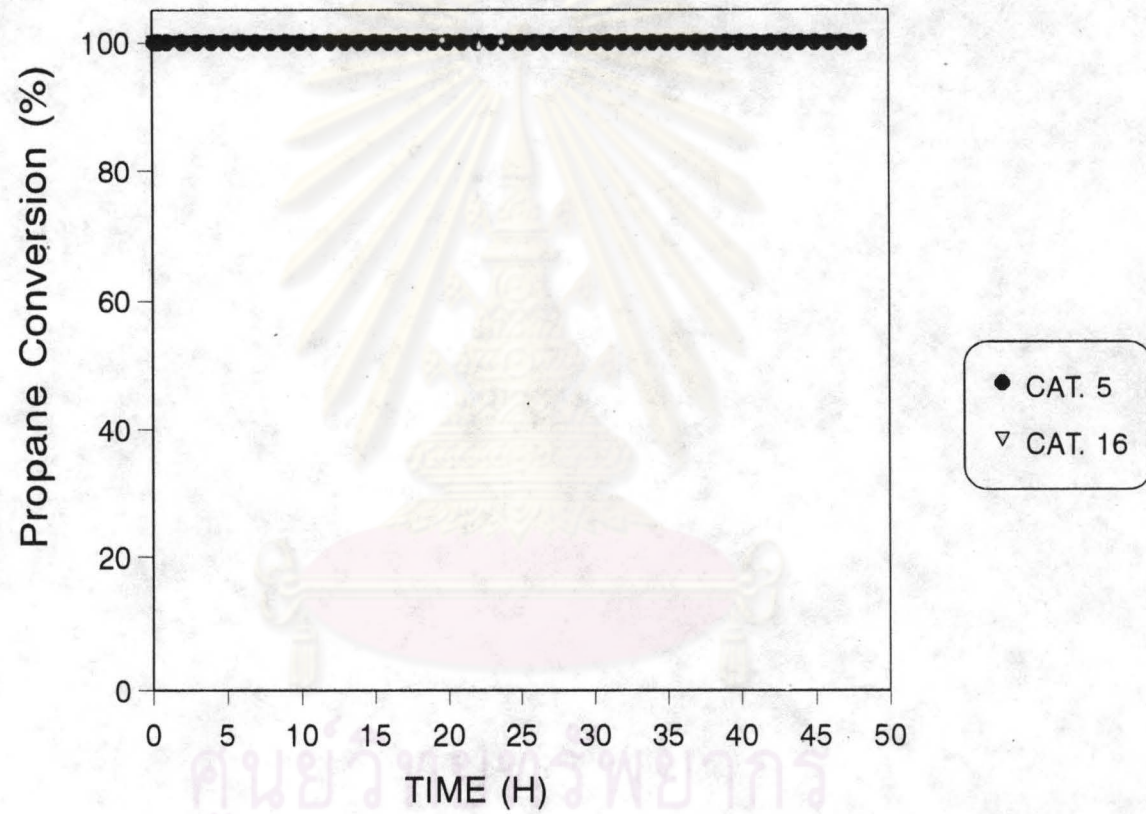


Figure 5.14 Effect of time on stream on Propane conversion of CAT. 5 and CAT. 16. Condition aging 48 h. at 600 °C  
Stoichiometric Number = 1.

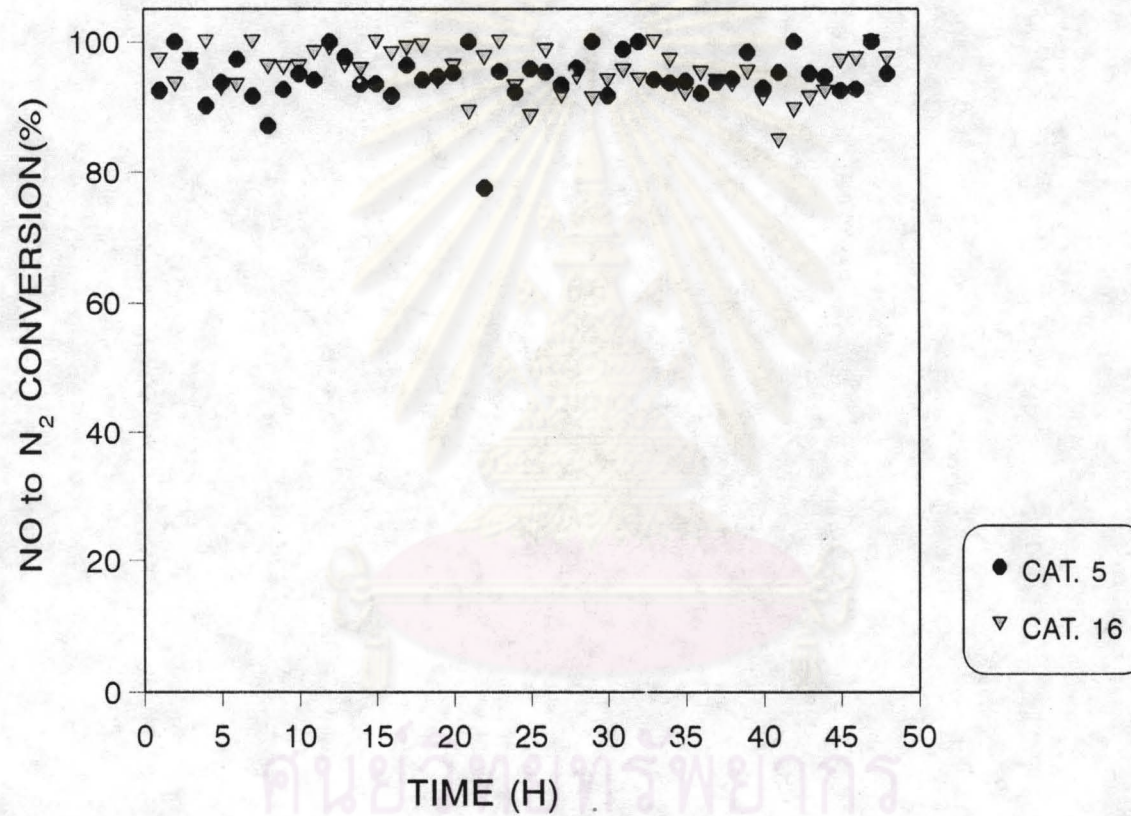


Figure 5.15 Effect of time on stream on NO conversion of CAT. 5 and CAT. 16. Condition aging 48 h. at 600 °C  
Stoichiometric Number = 1.

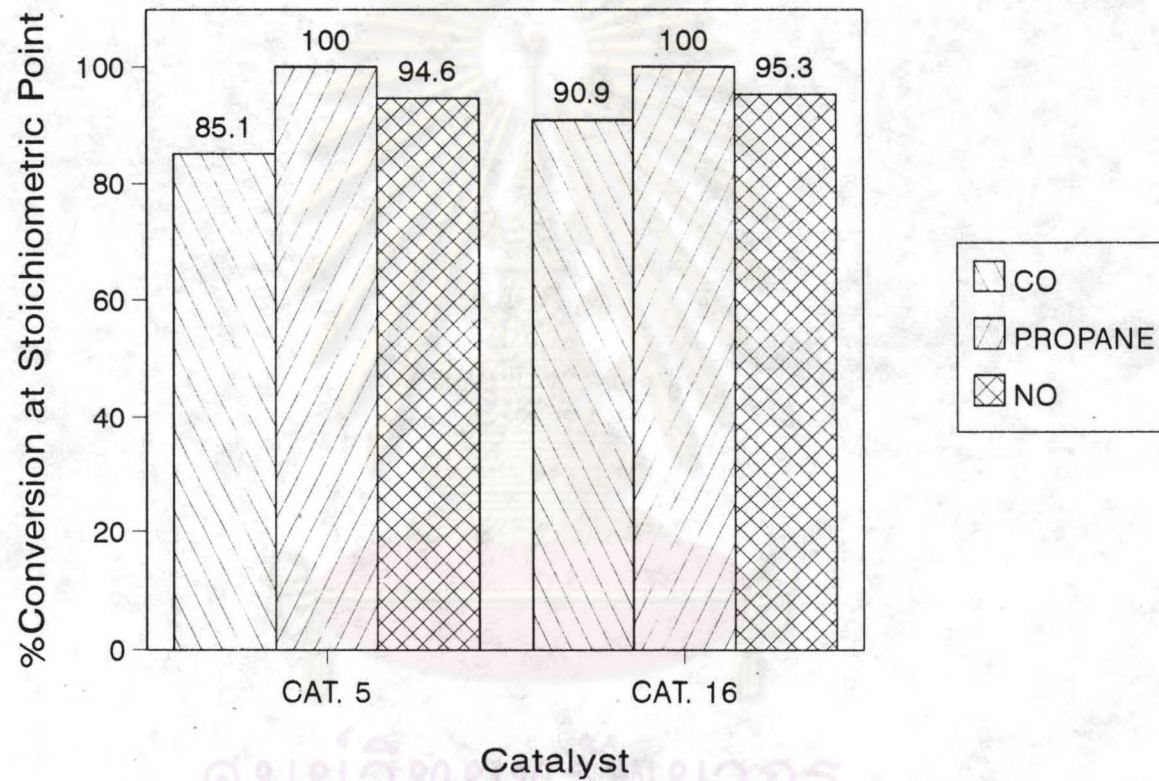


Figure 5.16 Comparison of the catalytic performance between CAT. 5 and CAT. 16 at 600 °C after aging 48 h. at 600 °C.

### 5.3.2 Effect of simulated A/F ratio on Catalytic Performance.

This experiment involved an investigation of the conversion efficiency of CO, C<sub>3</sub>H<sub>8</sub>, and NO as a function of stoichiometric number. The activity at a sample temperature of 500 °C was measured at different gas compositions. The gas compositions were characterized by the stoichiometric number (S).

Table 5.12 The gas compositions.

	S - value						
	0.67	0.72	0.897	0.98	1.05	1.31	1.45
Gas							
O <sub>2</sub>	0.96	0.94	1.07	1.35	1.37	1.75	1.97
CO	0.30	0.30	0.30	0.30	0.30	0.30	0.30
NO	0.05	0.05	0.05	0.05	0.05	0.05	0.05
C <sub>3</sub> H <sub>8</sub>	0.264	0.241	0.214	0.251	0.235	0.241	0.245
He	balance	balance	balance	balance	balance	balance	balance

As shown in figure 5.17, it appears clearly that the catalyst needs to operate close to the stoichiometric point in order to effectively convert simultaneously the pollutants. On the rich side the limiting factor was the CO conversion and on the lean side it was the NO conversion. In oxygen-deficient atmosphere, propane can be partially oxidized into carbon oxides and hydrogen on PtRh/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts at 330 - 550 °C. H<sub>2</sub> was formed by steam reforming (slow reaction) and water - gas shift (fast reaction) appeared in the reaction products after the complete disappearance of O<sub>2</sub> in

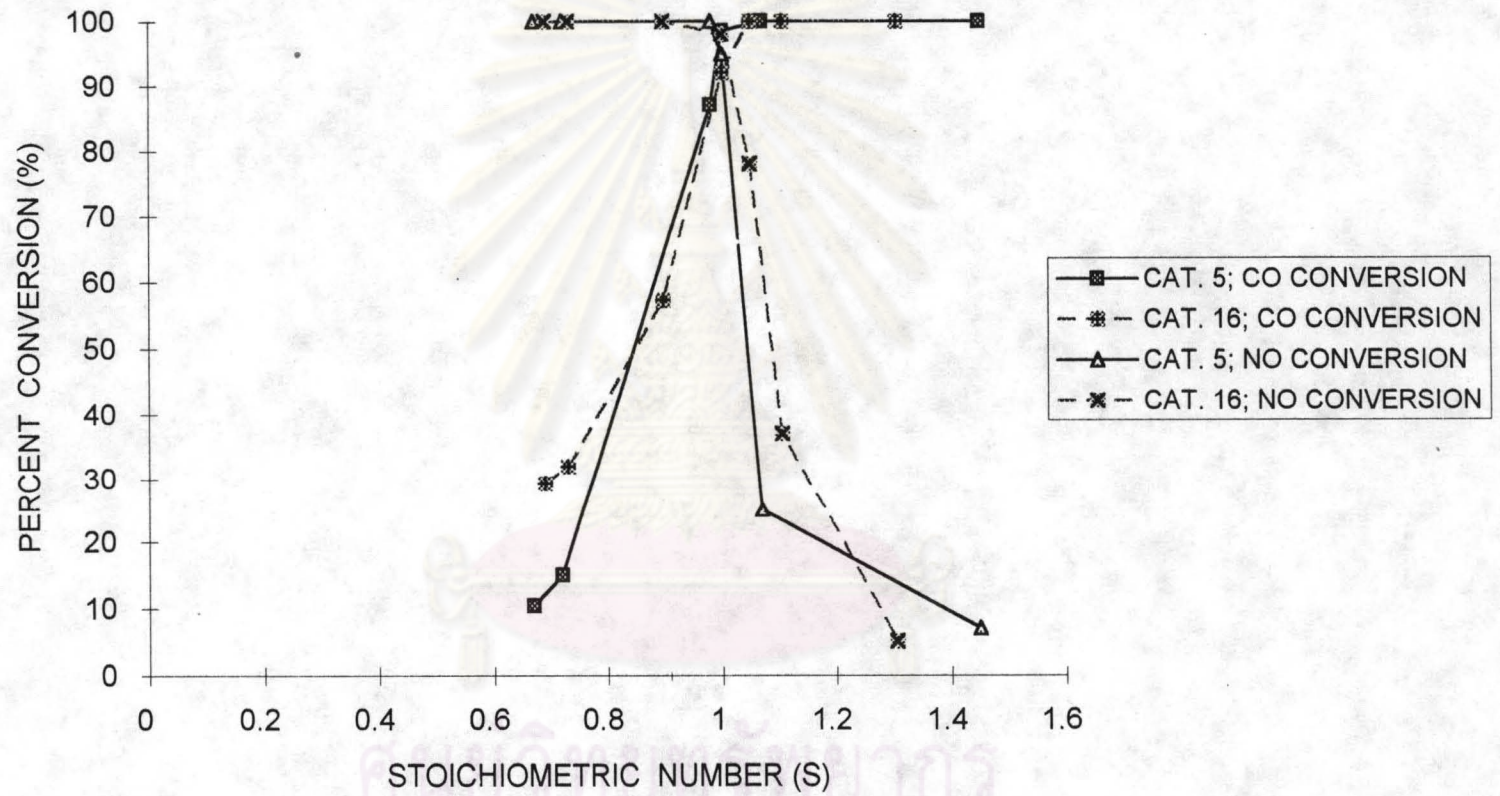


Figure 5.17 Effect of A/F ratio on CO and NO conversion for CAT. 5 and CAT. 16 at 500 °C and GHSV = 15,000 h<sup>-1</sup>  
Stoichiometric Number = 1.

the gas phase. Rhodium was the key component of the catalyst for the formation of  $H_2$  [19]. And from results in previous paper [48], rhodium can support water - gas shift reaction and steam reforming. It could widen the catalyst's window. The definition of window here is the A/F range that could convert all pollutants more than 80% conversion. Table 5.13 shows the amount of hydrogen formed from steam - reforming and water - gas shift reactions. Both reactions could enhance the CO conversion of various catalysts.

Table 5.13 The amount of hydrogen formed on rich side (0.67 - 0.897).  
(arbitrary unit)

Catalyst Sample	S-value			
	0.67	0.69	0.73	0.897
CAT. 5	516	430	-	-
CAT. 16	-	-	513	354

As can be seen in figure 5.29, the modified catalyst had higher performance on both CO and NO conversion than the conventional three - way catalyst. The window of the modified catalyst was  $1 \pm 0.03$  while that window of conventional catalyst was  $1 \pm 0.02$ .



#### 5.4 Effect of Catalyst Pretreatment on Performance of catalyst.

For the purpose of elucidation, the effect of catalyst pretreatment for the removal of three pollutants was described here. From the previous section, the best catalyst was the catalyst calcined in reducing atmosphere at 700 °C. In this section, the modified catalyst was further developed to attain a maximum performance. Fresh catalyst was prepared by the method similar to that used for CAT. 5, but after impregnating Pt metal, the catalyst was not calcined in any atmosphere. After that, fresh catalyst was pretreated in simulated exhaust gas atmosphere.

The fresh catalysts were pretreated in several atmospheric conditions such as :

- in air condition at 500 °C
- in rich condition of simulated exhaust gas at 700 °C;
- in stoichiometric condition of simulated exhaust gas 700 °C.

After pretreatment, catalyst efficiencies for emission control of exhaust gas were measured during temperature range of 150-700 °C.

Figures 5.18, 5.19, and 5.20 exhibit activities for CO oxidation, C<sub>3</sub>H<sub>8</sub> combustion and NO reduction, respectively. All of pretreatment conditions of each catalyst are shown in table 5.14.

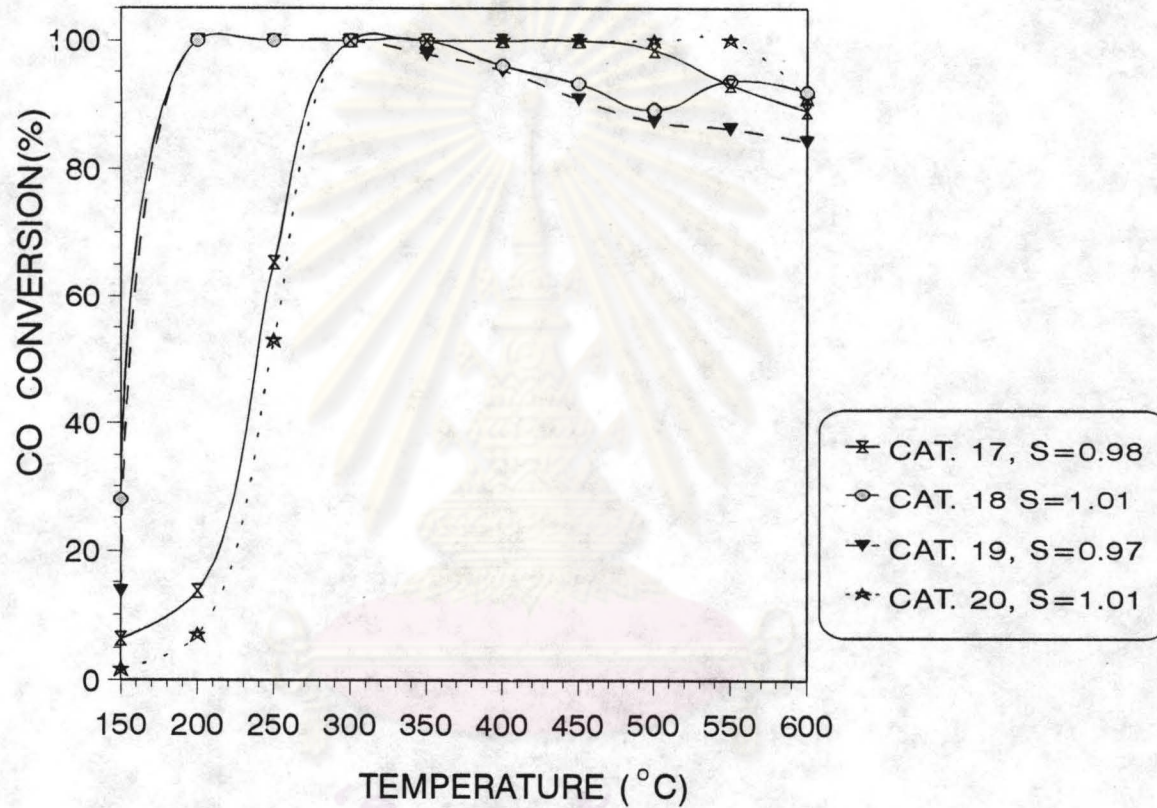


Figure 5.18 Effect of the pre-treatment condition on conventional catalysts

for CO Conversion :

pre-treated condition - CAT. 17  $S_1 = 0.68$

$S_2 = 1.00$

GHSV =  $15,000^{-1}$ . - CAT. 18  $S_1 = 1.00$

$S_2 = 1.00$

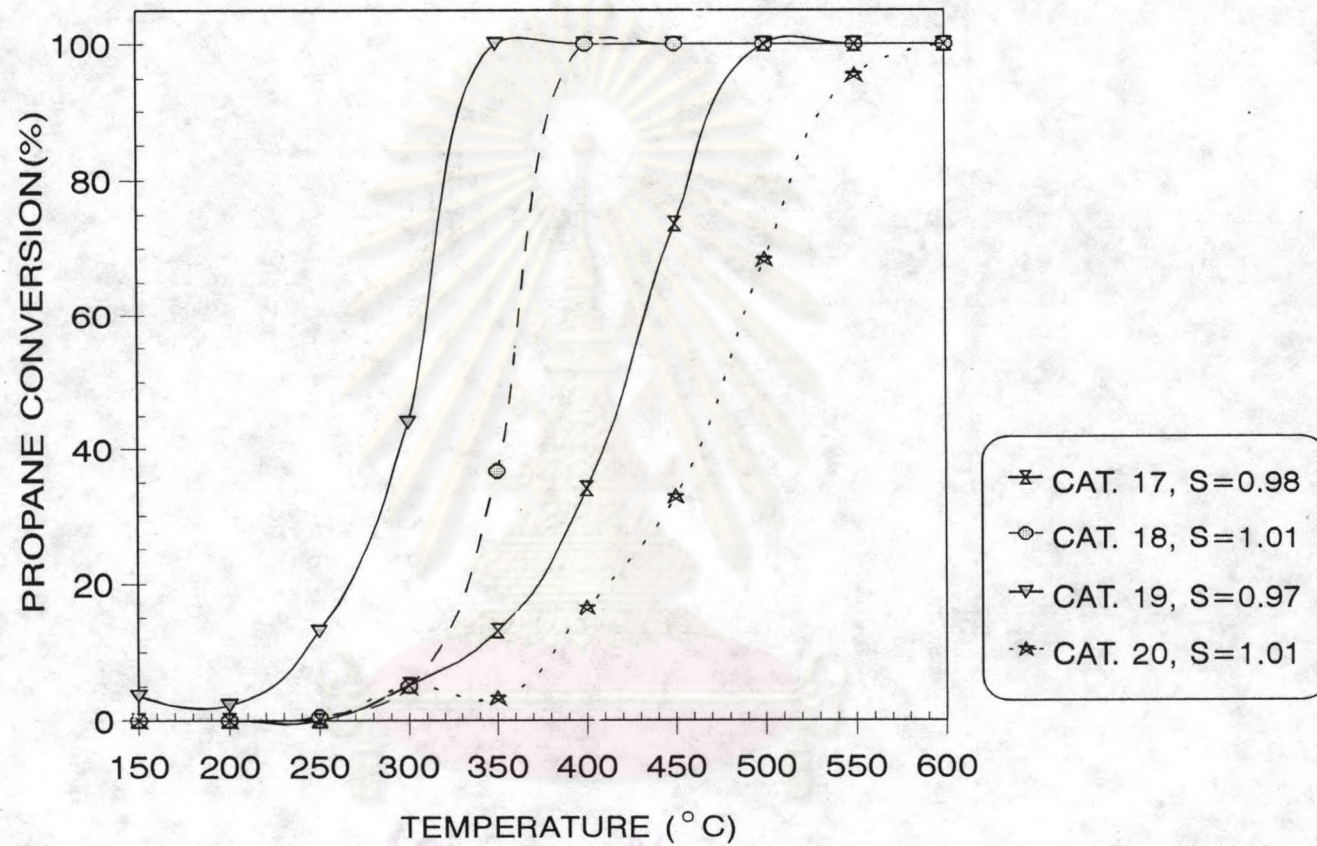


Figure 5.19 Effect of the pre-treatment condition on conventional catalysts for Propane Conversion :

pre-treated condition - CAT. 17  $S_1 = 0.68$

$S_2 = 1.00$

GHSV =  $15,000 \text{ h}^{-1}$  - CAT. 13  $S_1 = 1.00$

$S_2 = 1.00$

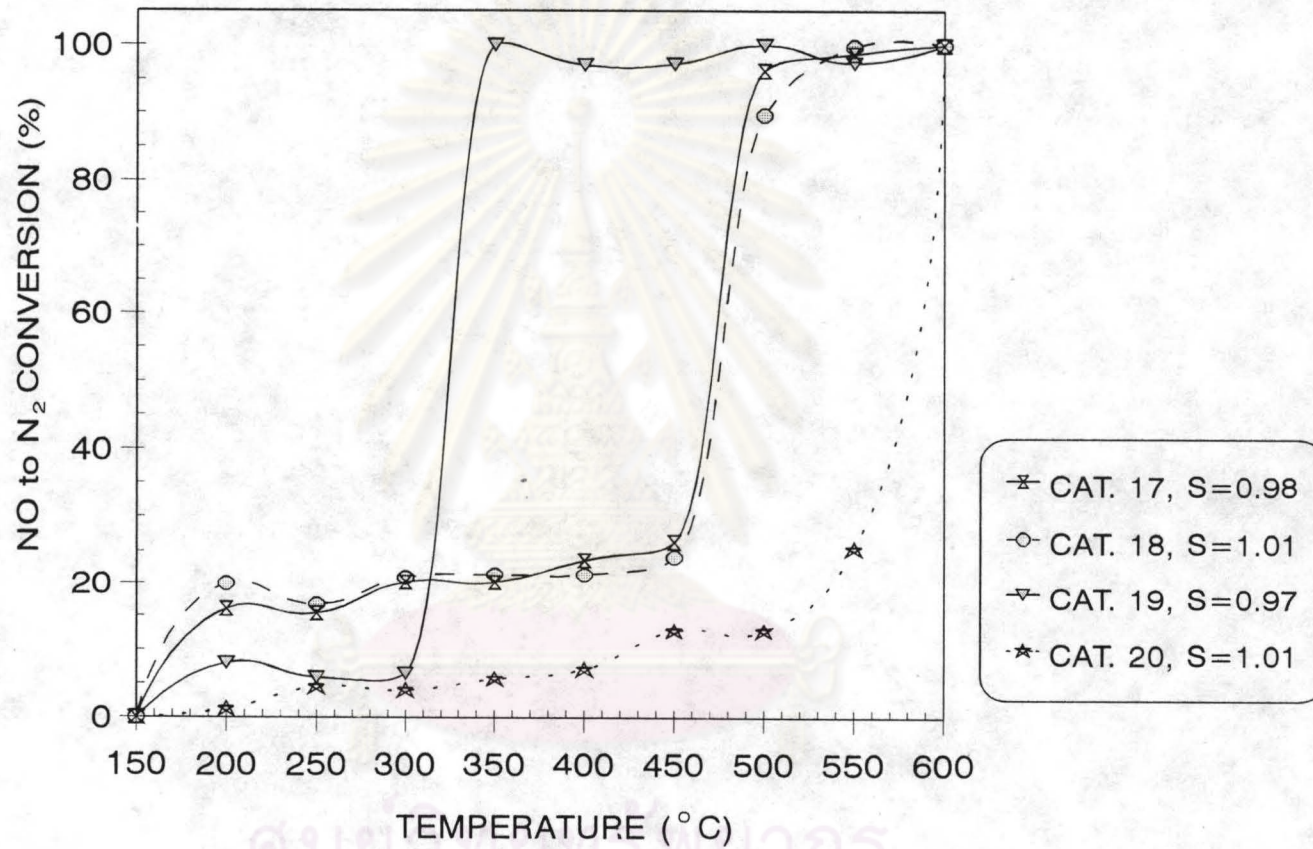


Figure 5.20 Effect of the pre-treatment condition on conventional catalysts for NO Conversion :

pre-treated condition	- CAT. 17	$S_1 = 0.68$
		$S_2 = 1.00$
GHSV = $15,000^{-1}$ .	- CAT. 18	$S_1 = 1.00$
		$S_2 = 1.00$

Table 5.14 The catalysts used in this part.

Catalyst	Pretreatment Condition
CAT. 17	Calcined in air at 500 °C
CAT. 18	Calcined in 10%H <sub>2</sub> at 700 °C
CAT. 19	S <sub>1</sub> = 0.68 (rich condition) S <sub>2</sub> = 1.00
CAT. 20	S <sub>1</sub> = 1.00 (stoichiometric) S <sub>2</sub> = 1.00

From these results, it can be summarized that CAT. 19 exerted the highest efficiency and activity, considering from the temperatures at which the catalyst attained the highest activity which was the lowest for CAT. 19. Whereas, CAT. 20 exhibited the lower efficiency than CAT. 17.

Table 5.15 The light - off temperature of pretreated catalysts.

Catalyst	Light - off Temperature (°C)		
	CO	Propane	NO
CAT. 17	240	424	470
CAT. 18	155	351	375
CAT. 19	162	300	325
CAT. 20	240	426	565

Table 5.15 shows the light - off temperature (50% conversion). It clearly shows that CAT. 19 gave the maximum activity at the lowest overall light-off temperature. For this reason, CAT. 19 exhibited the highest efficiency.

Table 5.16 Comparison of the active site among CAT. 17, CAT. 18, and CAT. 19.

Catalyst	Active Site (CO molecule/g.cat.)
CAT. 17	$1.78 \times 10^{18}$
CAT. 18	$0.514 \times 10^{18}$
CAT. 19	$0.389 \times 10^{18}$

The active site measurement in Table 5.16 can confirm the size of metal which was increased. The increase of metal size can be affected from SMSI phenomena.

From the data described above, it can be suggested that the pretreatment condition in rich exhaust gas was similar to reducing atmosphere. This method was the same as the modification of conventional three-way catalyst. However, the pretreatment method can give the higher efficiency.

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## Conclusion

The best catalyst was the pretreated catalyst in rich condition at 700° C for 7 hours (CAT. 19).

From the experimental results explained in each section it can be concluded that the best catalyst was CAT. 19 comprising of 9 wt%Ce-0.01 wt%Rh-0.03 wt%Pt and its preparations were as follows :

1. Loading Ce salt on  $\gamma\text{-Al}_2\text{O}_3$  , and then calcined.
2. Impregnating with Rh salt, and then calcined.
3. Finally, reimpregnating with Pt salt in form of chloroplatinic acid.



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