

## CHAPTER V

### RESULTS AND DISCUSSIONS

In this research, new compositions of base metals, for the reduction and oxidation reactions of three pollutants from simulating automotive exhaust gases are proposed. All reactions were performed at stoichiometric composition.

The results and discussions are presented in five parts as follows :

#### **5.1 Effect of screening metal on the catalytic activity.**

There are some obvious disadvantages in the use of a noble metal catalyst. They are relatively scarce and expensive and their operation requires a strict air/fuel ratio control and a low amount of metal present and is also relatively sensitive to impurities. (Stegenga,1991) For this reason, the development of non-noble metal alternatives was investigated. The components of catalysts are dealt with in previous studies.(Pannee,1995) The cerium significantly enhances NO<sub>x</sub>, CO and HC performance near stoichiometric air/fuel (A/F) ratio, improves resistance to thermal loss of BET surface area of the alumina support, stabilizes the active precious metal in a finely dispersed state, and also enhances the water gas shift reaction for the removal of CO under O<sub>2</sub>- deficient condition. (Yao and Yao, 1984) Due to the advantages of cerium oxide above, cerium was proposed for use in the modified three way catalyst.

In screening the modified catalysts, the method of scientific approval which lead to finding the modified catalyst that has natural properties similar

to the conventional three-way catalyst was used. Ogata reported that  $Mg^{2+}$  ionic constitutes on supported palladium catalysts would enhance the decomposition activity at  $550^{\circ}$  - $750^{\circ}$  C. In this review, magnesium was used as a substitute for rhodium in the conventional three-way catalyst whereas platinum was fixed or was replaced by palladium. Table 5.1 shows the name of modified three-way catalysts (as CAT.A, CAT.B).

Table5.1 Names of base metal supported catalysts.

NAME	COMPOSITION OF CATALYSTS
1. CAT. A	9%Ce-15.0%Mg-0.03%Pt
2. CAT. B	9%Ce-0.01%Mg-0.03%Pd
3. CAT. C	9%Ce-0.01%Ga-0.03%Mo
4. CAT. D	9%Ce-0.01%Fe-0.03%Rh
5. CAT. E	9%Ce-0.01%Co-0.03%Pd
6. CAT. F	9%Ce-0.01%Rh-0.03%Pt
7. CAT. G **	H-ZSM-5 Zeolite
8. CAT. H	9%Ce-0.01%Ni-0.03%Ag
9. CAT. I	9%Ce-0.01%Cu-0.03%Pd
10. CAT. J	9%Ce-0.01%Cu-0.03%Cd

Remark: \*\* is a catalyst whose performance was tested by the de- $NO_x$  reaction.

Then all of the catalysts were subject to redox reaction. In this study, the criterion for comparative activity of the catalyst is the light-off temperature

index ( $T_{50}$ ). It is defined as the temperature which achieved 50% conversions of NO, CO and propane. (Shelef,1968) From figure 5.1, each catalyst has a different light-off temperatures which is used to compare the activity of catalyst in further discussion. The light-off temperatures of NO conversion were plotted with the atomic mass ratio of metal supported catalysts, which is shown in figure 5.2. It was demonstrated that the light-off temperature trend decreases with a lower atomic mass ratio number and light-off temperature increases with an higher atomic mass ratio number. To confirm these relations, the light-off temperature of the conventional three-way catalyst (CAT.F) and H-ZSM-5 zeolite (CAT.G) catalyst were compared. It was found that this correlation is greatly supported by both catalysts. Subsequently, the catalysts which have an atomic mass ratio lower than the conventional three-way catalysts were prepared in order to prove the proposed correlation. Those catalysts are CAT.C to CAT.E and CAT.H to CAT.I which are shown in table 5.1. It was illustrated that when atomic mass ratio was close to CAT.F, and it has a light-off temperature close to conventional three-way catalyst. It seems that those catalysts exhibit similarly to the CAT.F. The subsequent work in this paper pertains only to the use of CAT.E as a modified three-way catalyst for further study. CAT.E is in a group 8B, having an atomic mass ratio nearest to CAT.F and the light-off temperature was lower than CAT.F by 10°C. Figures 5.3 and 5.4 show CO, propane conversion. It can be seen that the activities of catalysts changed as a function of temperature. In figure 5.3, the CO conversion was divided into two groups. Group one in a lower temperature range achieves 100% conversion is around 300° or 350°C while the higher temperature range

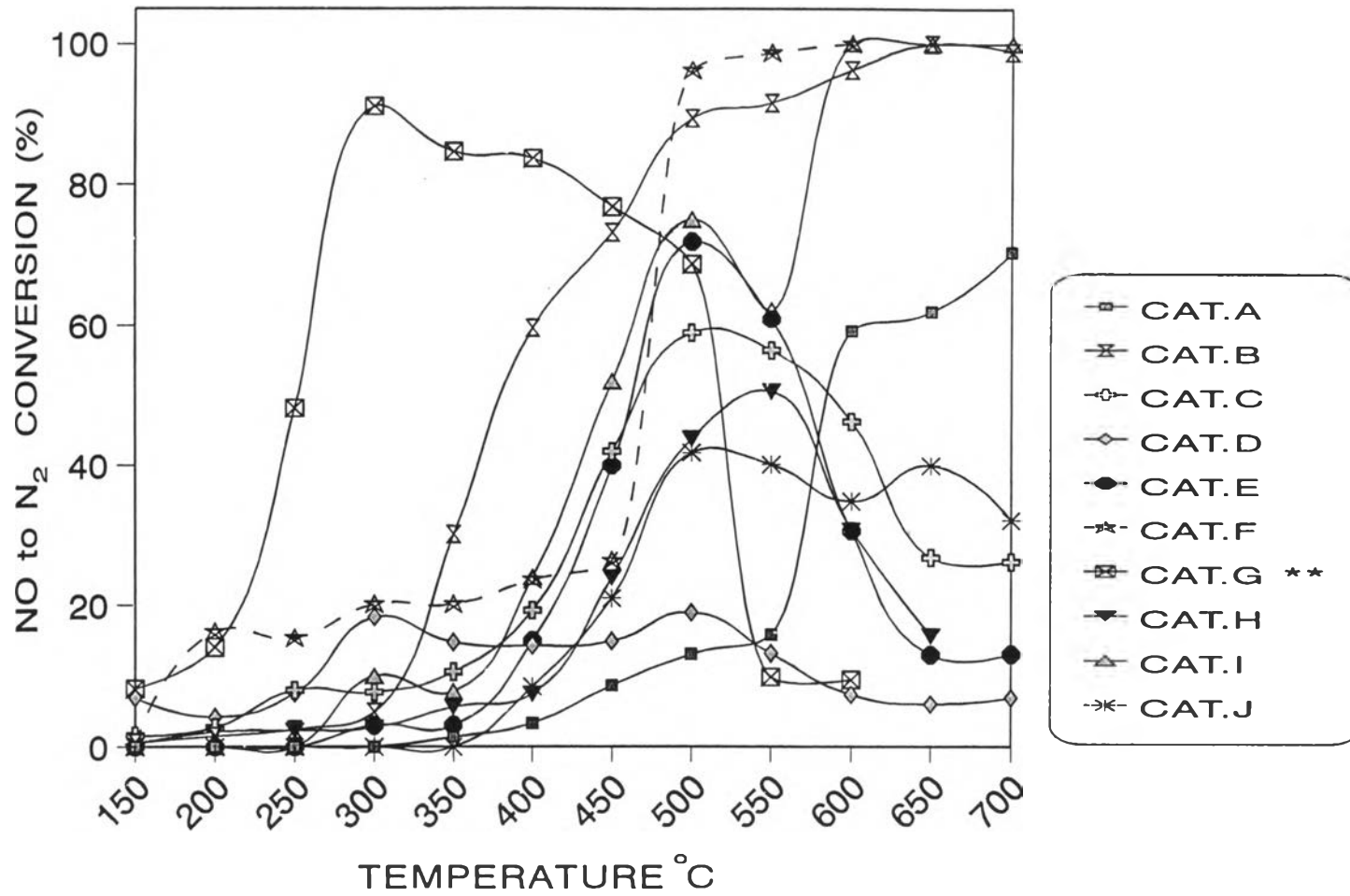


Figure 5.1 Temperature dependence of NO conversion on various metal-loaded alumina. GHSV=15,000 h<sup>-1</sup>  
 feed composition at stoichiometric (S<sub>2</sub>=1.0)

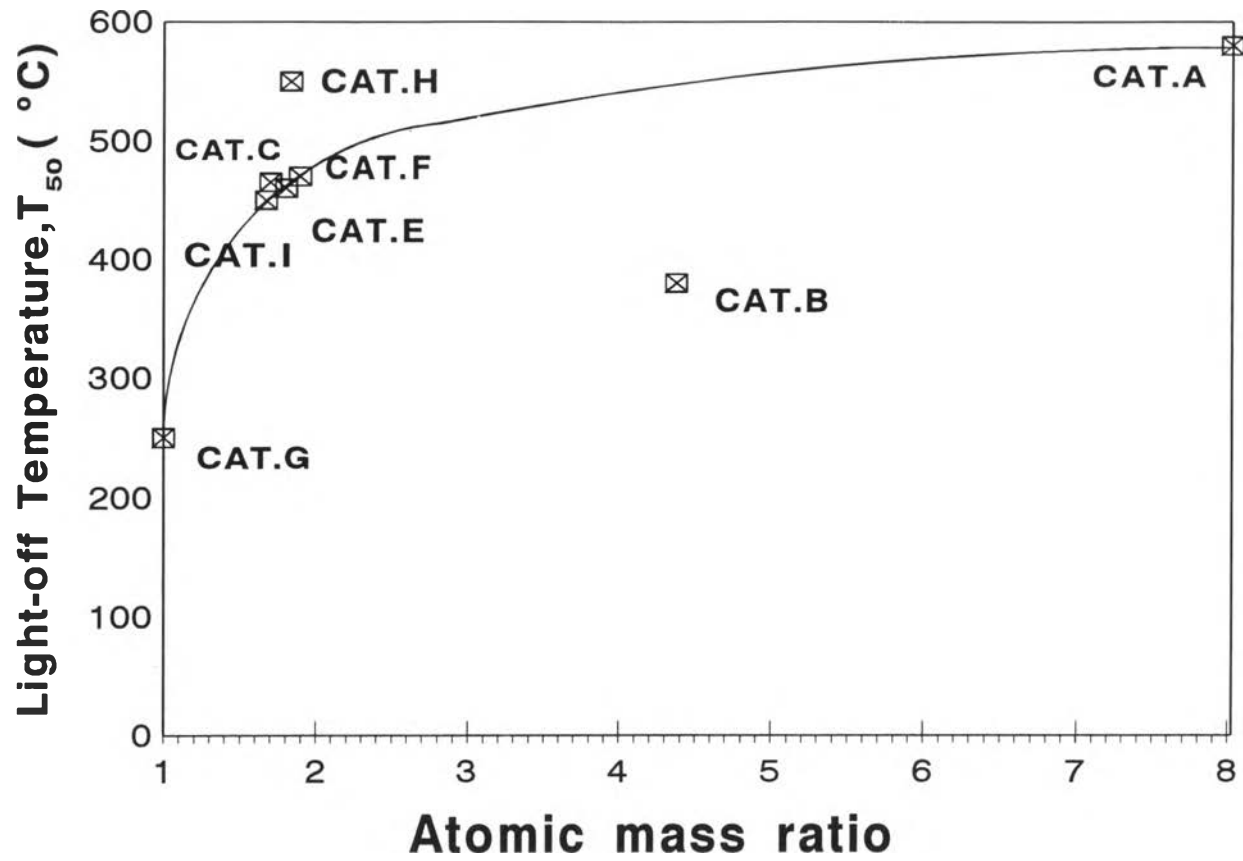


Figure 5.2 The light - off temperature of NO to N<sub>2</sub> conversion(%) versus the atomic mass ratio of oxidizing metal to reducing metal.

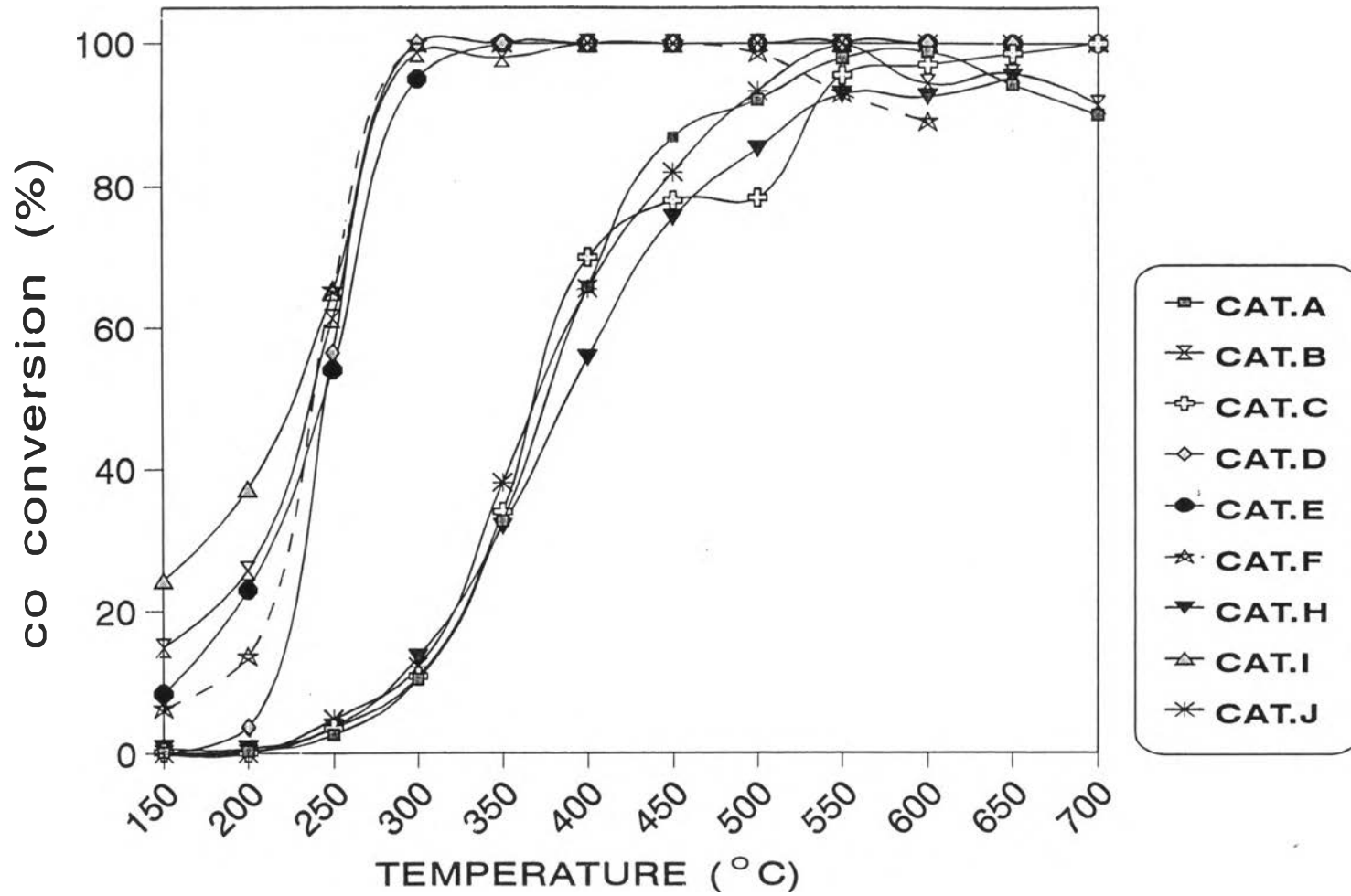


Figure 5.3 Temperature dependence of CO conversion of various metal-loaded alumina. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

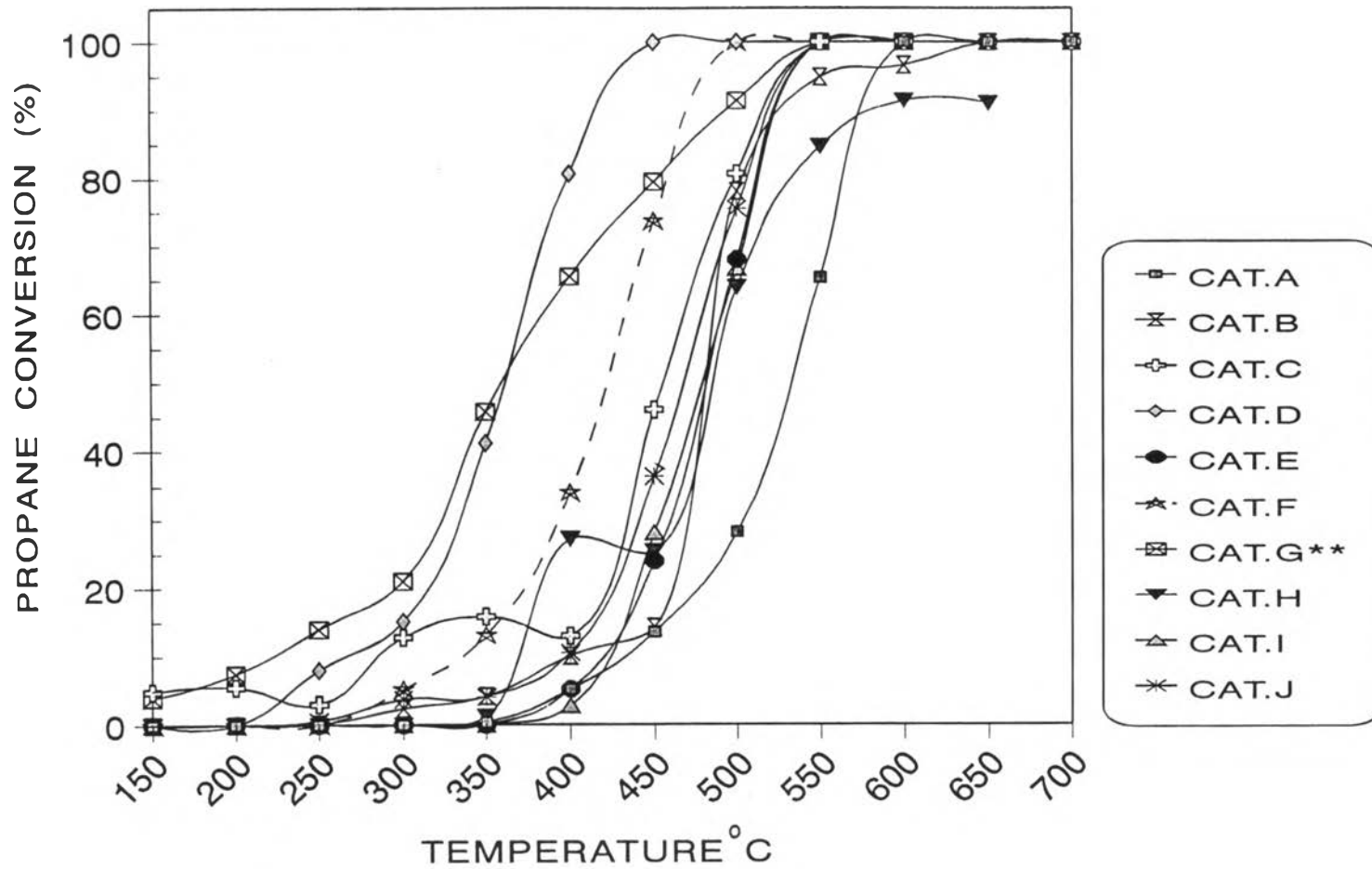


Figure 5.4 Temperature dependence of propane conversion of various metal-loaded alumina. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

group attains 100% conversion at high temperature (from 550-700° C), and some catalysts could not achieve 100% conversion in this temperature range. However, CAT.E also exhibits similarities with CAT.F. For propane conversion, most catalysts have a light-off temperature in the range 455-485°C, except CAT.D and CAT.G which show lower light-off temperatures than CAT.F.

In summary, the replacement of the conventional three-way catalyst by modified one was scientifically searched by adopting the atomic mass ratio as the parameter for catalyst selection. The modified three-way catalyst studied here, Ce-Co-Pd, was in the same group with the approximately same atomic mass ratio to that of the conventional one.

## **5.2 Effect of Pd /Co ratio on catalytic performance.**

In this part, catalysts with different Pd/Co ratio were studied. The range of Co metal content was varied between 0.003-0.03% by weight while the Pd content was fixed at 0.03% by weight. This range of catalyst composition was found to be able to achieve high activity. Table 5.2 shows the compositions of the catalysts used in this part.



Table 5.2 The catalysts of various Pd/Co ratios.

NAME	COMPOSITION OF CATALYSTS	RATIO OF Pd/Co
CAT.1	9%Ce-0.03%Co-0.03%Pd	1:1
CAT.2	9%Ce-0.015%Co-0.03%Pd	2:1
CAT.3	9%Ce-0.01%Co-0.03%Pd	3:1
CAT.4	9%Ce-0.005%Co-0.03%Pd	6:1
CAT.5	9%Ce-0.003%Co-0.03%Pd	9:1

The prepared catalysts were tested by redox reaction using simulated exhaust gas at stoichiometric number ( $S=1.0$ ) composition. The conversion of NO to  $N_2$  of palladium-cobalt catalysts is shown in figure 5.5. It was observed that NO conversion of all the catalyst are different at  $500^\circ\text{C}$ . The NO conversion can be ordered as follows : CAT.3 > CAT.4 > CAT.1 > CAT.2 ~~ CAT.5. The result indicates that the highest active catalyst is CAT.3. The effect of Pd/Co ratio on CO and propane is shown in figure 5.6 and 5.7, respectively. It can be observed that the variation of Pd/Co ratio insignificantly affects the CO and propane conversions. The results also show that CO conversion reach 100% at  $350^\circ\text{C}$  and propane conversion reach 100% at  $550^\circ\text{C}$  on most catalysts. In addition, the maximum conversions value of both conversions can be maintained until  $700^\circ\text{C}$

In addition, it was observed that all catalysts show insignificant difference in their light-off temperature for CO and propane conversions. The light-off temperature of CO conversion is around  $240^\circ\text{C}$  and of propane is around  $470^\circ\text{C}$ .

Table 5.3 The active site and BET surface area of catalysts calcining in air atmosphere.

Catalyst	Active site (CO molecule/g.cat.)	BET (m <sup>2</sup> /g.cat)
CAT.1	5.86 x 10 <sup>17</sup>	238.84
CAT.2	5.20 x 10 <sup>17</sup>	222.91
CAT.3	6.38 x 10 <sup>17</sup>	226.96
CAT.4	7.12 x 10 <sup>17</sup>	227.11
CAT.5	4.48 x 10 <sup>17</sup>	225.78

The active site data reported in table 5.3 above were obtained from the characterization by CO chemisorption. Figure 5.8 shows the relationship between active site of Pd/Co catalyst and %Co loading. The figure shows that the active site increases when increase %Co loading, but only in low %Co loading region. The highest active site value is obtained from CAT.4. The amount of active sites, however, was reduced when %Co loading was increased again upto about 0.015%. Beyond this point upto 0.03% only a slight increase was observed. The reduction of active site might be because palladium and cobalt combine each-other.

For comparison, the active sites of conventional three-way catalysts with different ratios of Pt/Rh (Pannee,1995) are plotted in figure 5.9. From figures 5.8 and 5.9 one can observe that the relationship between active site to %Rh loading of conventional three-way catalysts has similar behavior to the relationship between active site and %Co loading of Pd/Co catalyst. The explanation for this may be because Pd/Co can form alloy within a range of composition as what was observed in the case of Pt/Rh by Harrison (1978). The most active catalyst of Pt/Rh and

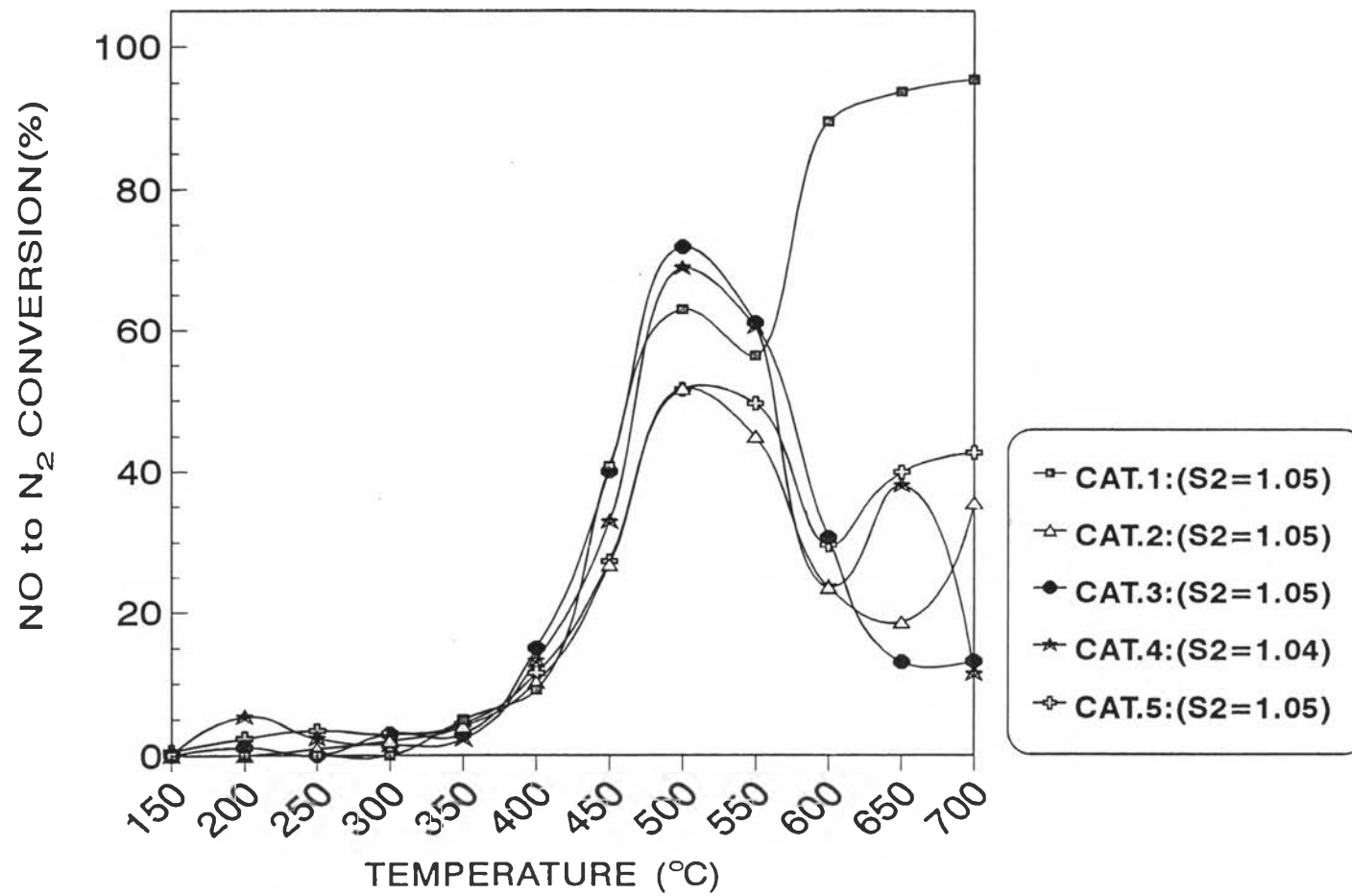


Figure 5.5 Effect of Pd/Co ratio for NO conversion on modified three-way catalysts. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

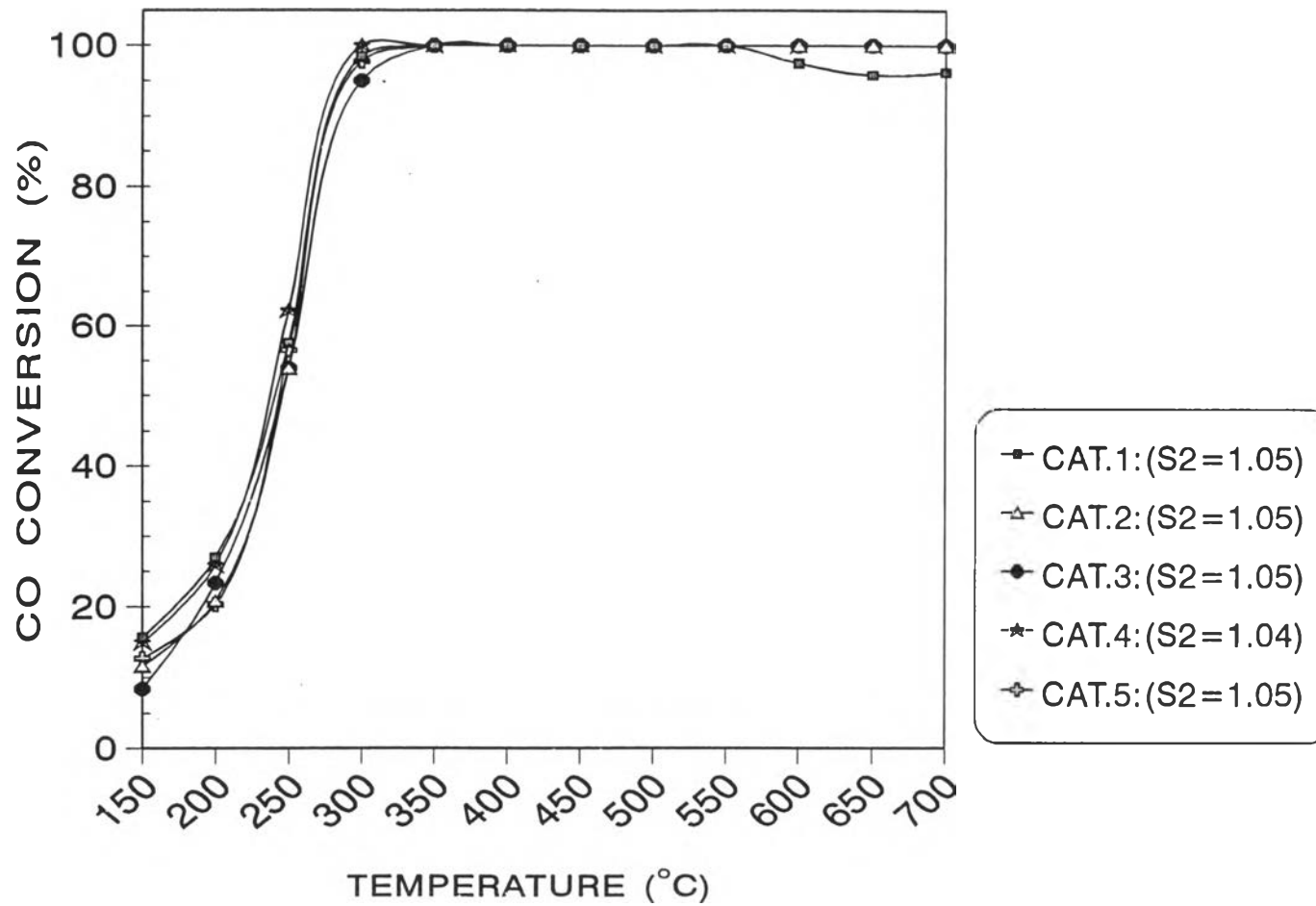


Figure 5.6 Effect of Pd/Co ratio for CO conversion on modified three-way catalysts. GHSV = 15,000 h<sup>-1</sup>  
 feed composition at stoichiometric (S<sub>2</sub> = 1.0)

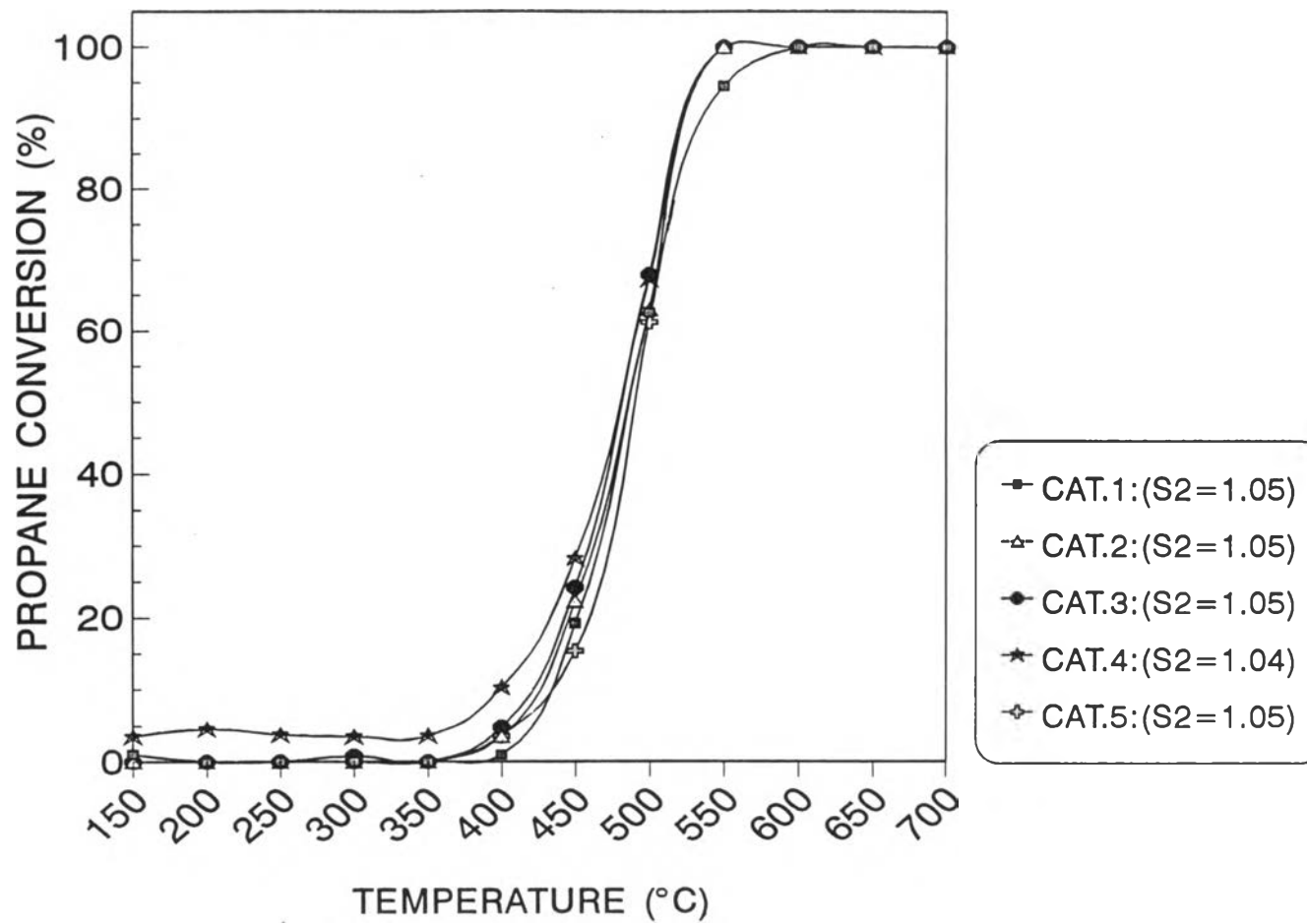


Figure 5.7 Effect of Pd/Co ratio for Propane conversion on modified three-way catalysts. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

Pd/Co is at the weight ratio of 3:1 (0.01 wt% Rh in case of conventional three-way catalyst, and 0.01 wt% Co in case of Pd/Co catalyst). But when the turn over number, TON, (defined as molecule of NO convert to N<sub>2</sub> per active site, Shatterfield 1991) of both catalysts is compared to each other, the result demonstrates that TON of modified three-way catalyst (Pd/Co) is higher than TON of the conventional three-way catalyst (Pt/Rh) as shown in figure 5.10. Therefore, it can be indicated that the strength of active site of modified three-way catalyst (Pd/Co) is more active than the active site of conventional three-way catalyst (Pt/Rh). The result of NO to N<sub>2</sub> conversion in figure 5.5 which shows that CAT.1, after reaching a maximum NO to N<sub>2</sub> conversion at 500°C, can still achieve higher conversion at higher temperature while the conversion of other catalysts begin to drop after reaching the maximum NO conversion at 500°C may be explained using the effect of increasing amount of Co beyond an optimal point.

In summary, CAT.1 is a suitable catalyst for NO reduction to N<sub>2</sub>. Because it is only catalyst which can achieve high NO to N<sub>2</sub> conversion over a wide range of temperature, though the CO and propane conversion of catalyst with different Pd/Co ratios is insignificantly different. In addition, it has been found that the state of partially mixed metal catalyst, was reflected by the early decrease in metal site, was required to exert the highest activity for NO conversion.

For BET surface area of different composition catalysts, they were observed that there are BET surface area closed to in each other. When it was led to compare to BET surface of bare support (as shown in appendix B), it is lower. Mainly because of plugged metal in pores of the bare support when the metal was loaded (Toyota,1991) and this lead to the reduction of the BET surface area.

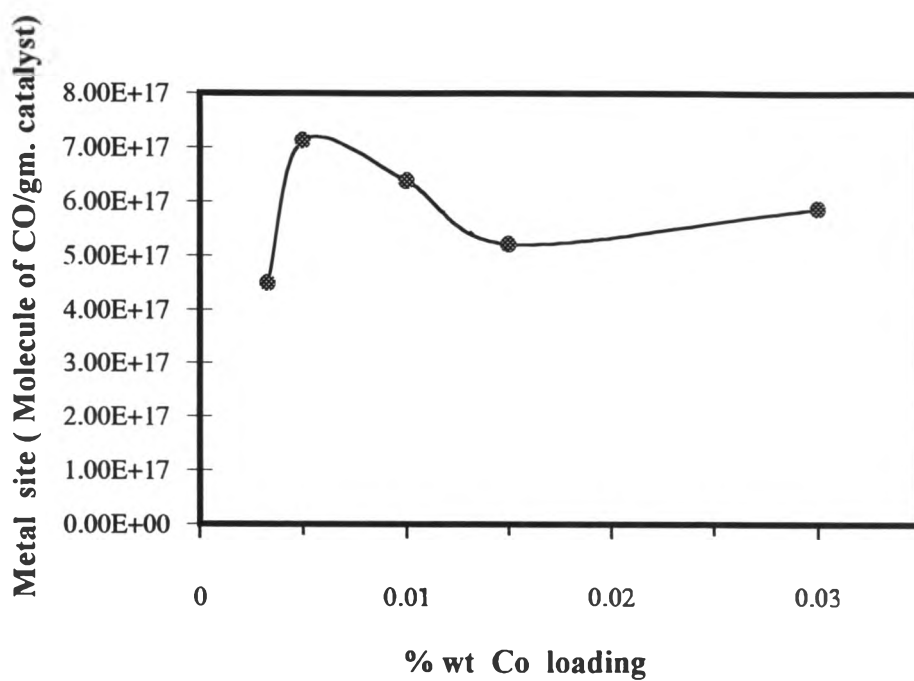


Figure 5.8 Shows metal site of modified three-way catalyst dependence on % Co loading.

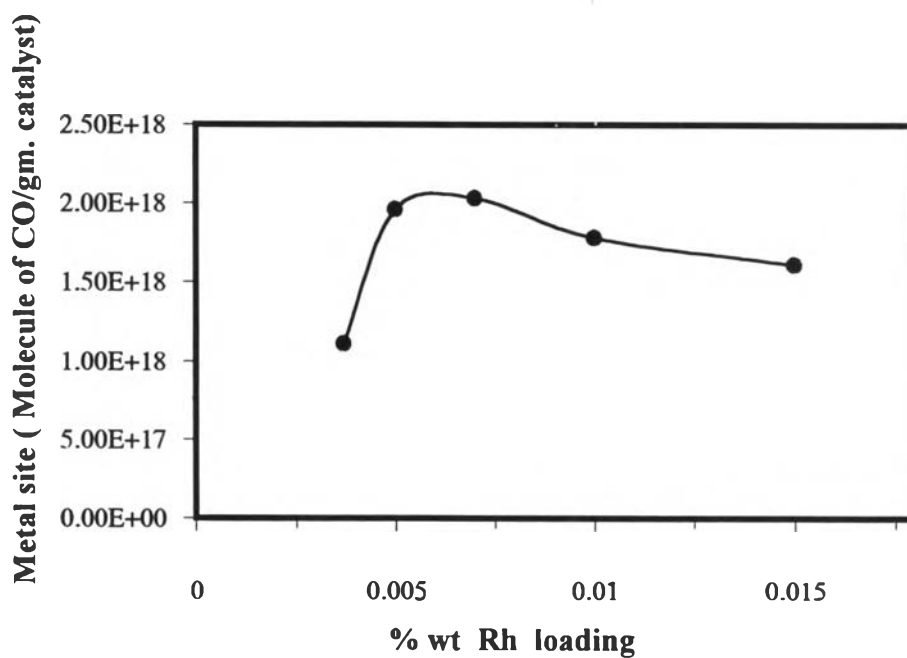


Figure 5.9 Shows metal site of conventional three-way catalyst dependence on % Rh loading.

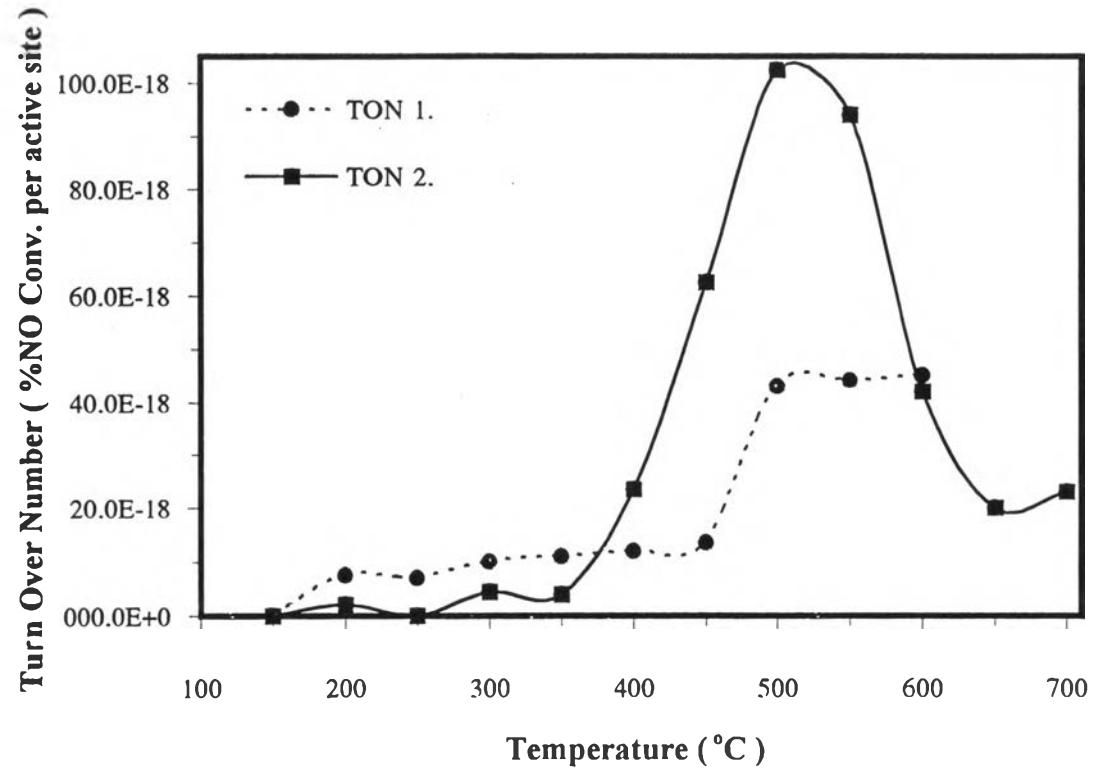


Figure 5.10 Show the turnover number of the conventional three-way catalyst

and modified three-way catalyst dependence on temperature.

TON 1 is turn over number of conventional three-way catalyst.

TON 2 is turn over number of modified three-way catalyst.



### 5.3 Effect of calcination in reducing atmosphere.

Much research investigates calcining atmosphere effect on efficiency and the activity of the catalyst. Pannee (1995) found that the modification of the conventional three-way catalyst was done by changing the calcining in air atmosphere to reducing atmosphere under high temperature. This shows an interesting influence on the efficiency of CO conversion and NO reduction. Huang (1991) reported that high temperature treatment in reducing atmosphere was beneficial to carbon monoxide oxidation while an oxidizing atmosphere was usually preferred for nitric oxide reduction using a copper catalyst. It should be interesting to see whether a similar feature is at work for modified three-way catalysts.

In this experiment, the information on studied catalysts is shown in table 5.4.

Table 5.4 The modified calcinating condition

NAME OF CATALYSTS	CALCINATION CONDITIONS
CAT. 1	Calcined in air at 500°C
CAT. 6	Calcined in 10%H <sub>2</sub> /N <sub>2</sub> at 400°C
CAT. 7	Calcined in 10%H <sub>2</sub> /N <sub>2</sub> at 500°C
CAT. 8	Calcined in 10%H <sub>2</sub> /N <sub>2</sub> at 600°C
CAT. 9	Calcined in 10%H <sub>2</sub> /N <sub>2</sub> at 700°C

The CAT.1 in the previous part was modified by calcination in a reducing (10% $H_2/N_2$ ) atmosphere at high temperature range of 400 - 700°C. The effect of these calcination conditions was studied by performance test.

NO conversion are illustrated in figure 5.11. The results indicated that the activity of CAT.6, 7 was higher than CAT.1. Influence of calcination temperature was obviously observed on CAT.6, CAT.7, NO conversion of them could be improved to 87% and 79% at 550°C. Eventhough the light-off temperature of CAT.6, CAT.7 is higher than CAT.1 about 20°C and 50°C, respectively. On the contrary, CAT.8 and CAT.9 show a negative effect after high temperature calcining in reducing atmosphere. The catalytic activity of them were suppressed .

For the activity of CO conversion was more improved than NO conversion (see in figure 5.12). At high calcination temperature (700°C), CO conversion attained 100% at only 250°C. While the calcination temperature was lower than 700°C (400-600°C), the temperature of maximum CO conversion (100%) shift up from about 250°C to about 300°C. When maximum temperature of CO conversion was compared to CAT.1, CAT.1 show the highest (350°C) maximum temperature. The temperature range of 500-700°C, the orders of CO conversion were :

$$\text{CAT.9} > \text{CAT.8} > \text{CAT.7} > \text{CAT.6} \sim \text{CAT.1}$$

From the descriptions of experimental data, it can suggest that influence of calcination in reducing reagent such as hydrogen may enhance the activity of catalyst. In addition, it can enhance the propane conversion which shown in figure 5.13. The maximum temperature (100%) is decreased from CAT.1 about 50°C and there is no different in series of temperature.

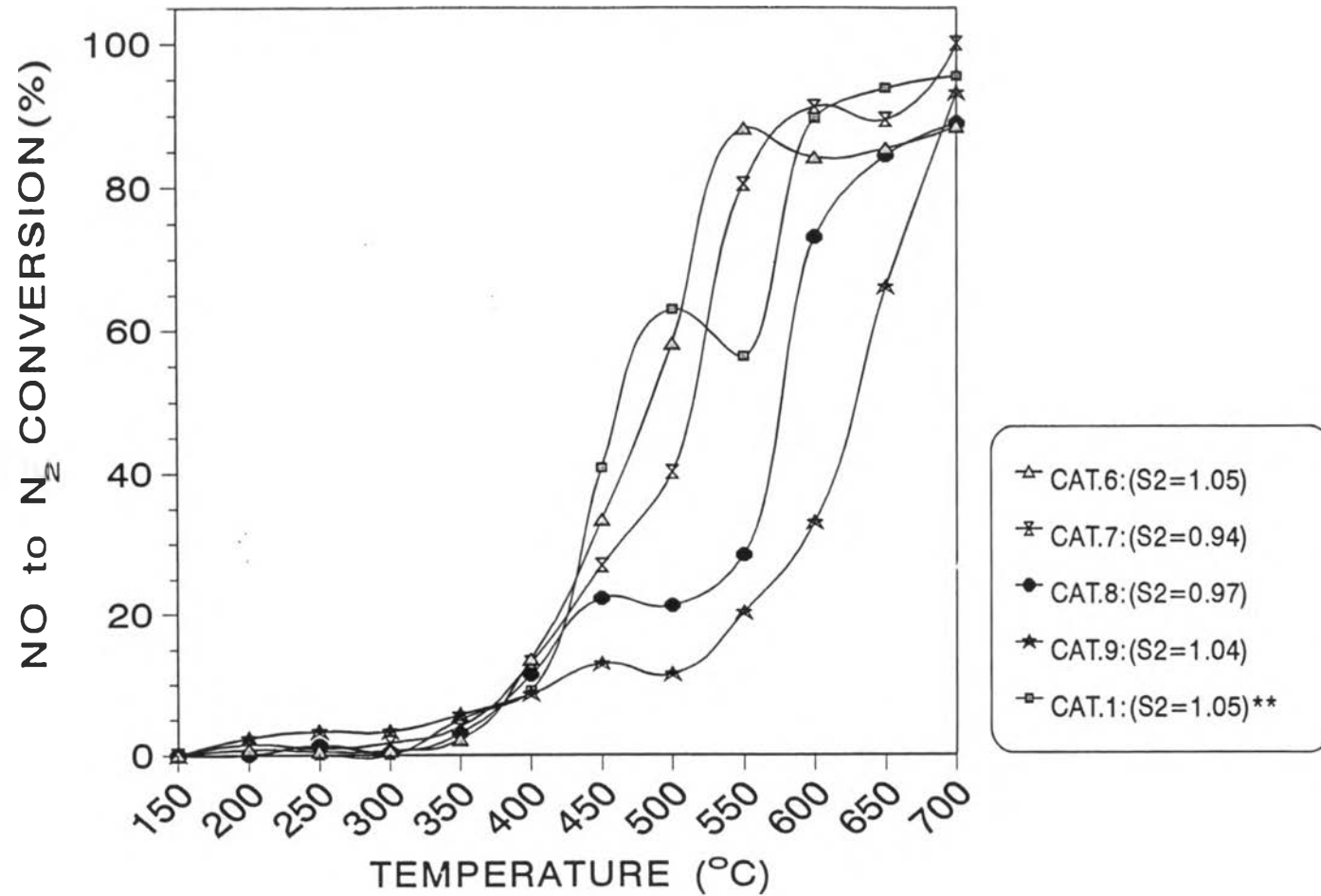


Figure 5.11 Effect of various temperature of calcination in reducing atmosphere on NO conversion in modified three-way catalysts. GHSV=15,000 h<sup>-1</sup>: feed composition at stoichiometric (S<sub>2</sub>=1.0)

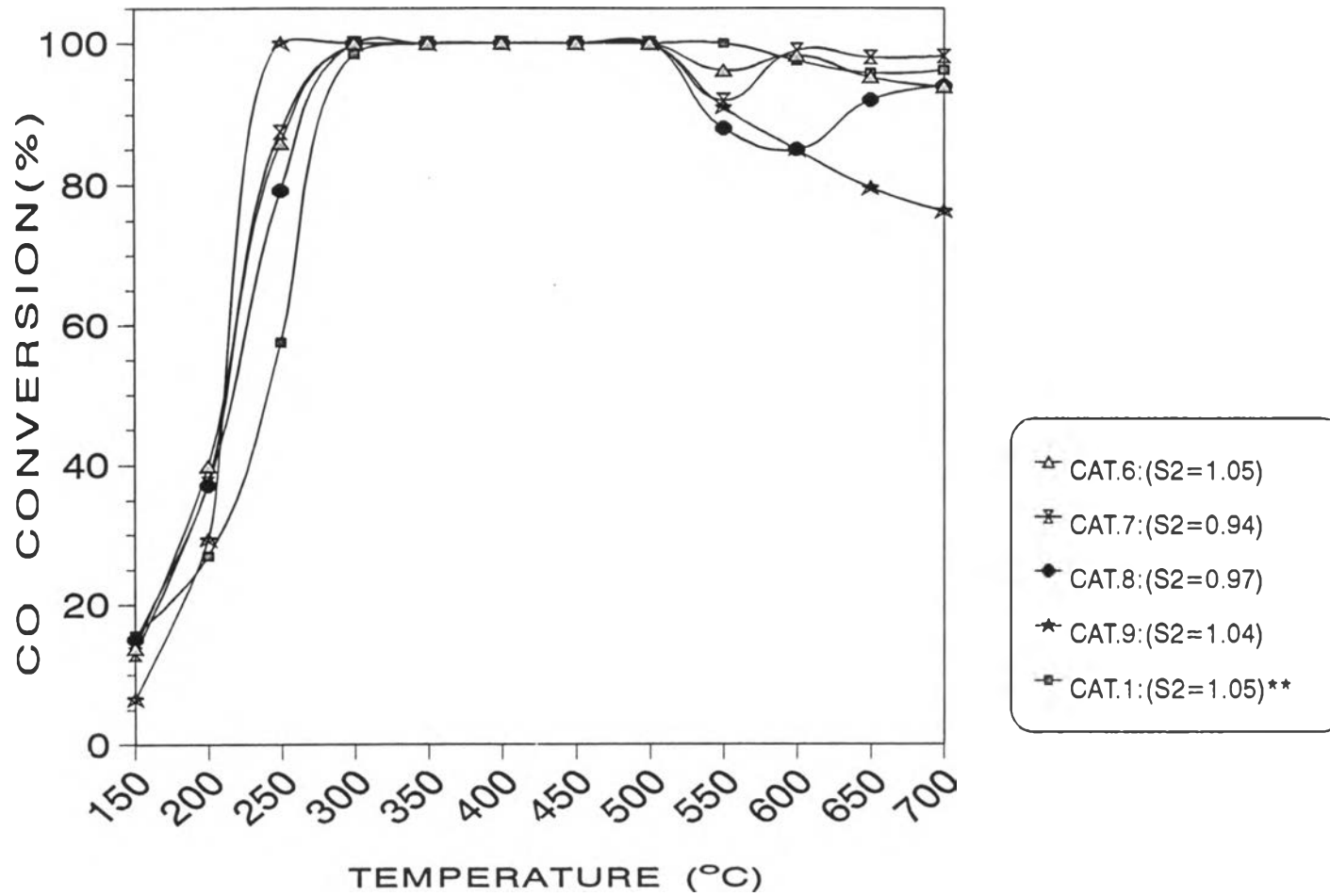


Figure 5.12 Effect of various temperature of calcination in reducing atmosphere on CO conversion in modified three-way catalysts. GHSV=15,000 h<sup>-1</sup>: feed composition at stoichiometric (S<sub>2</sub> = 1.0)

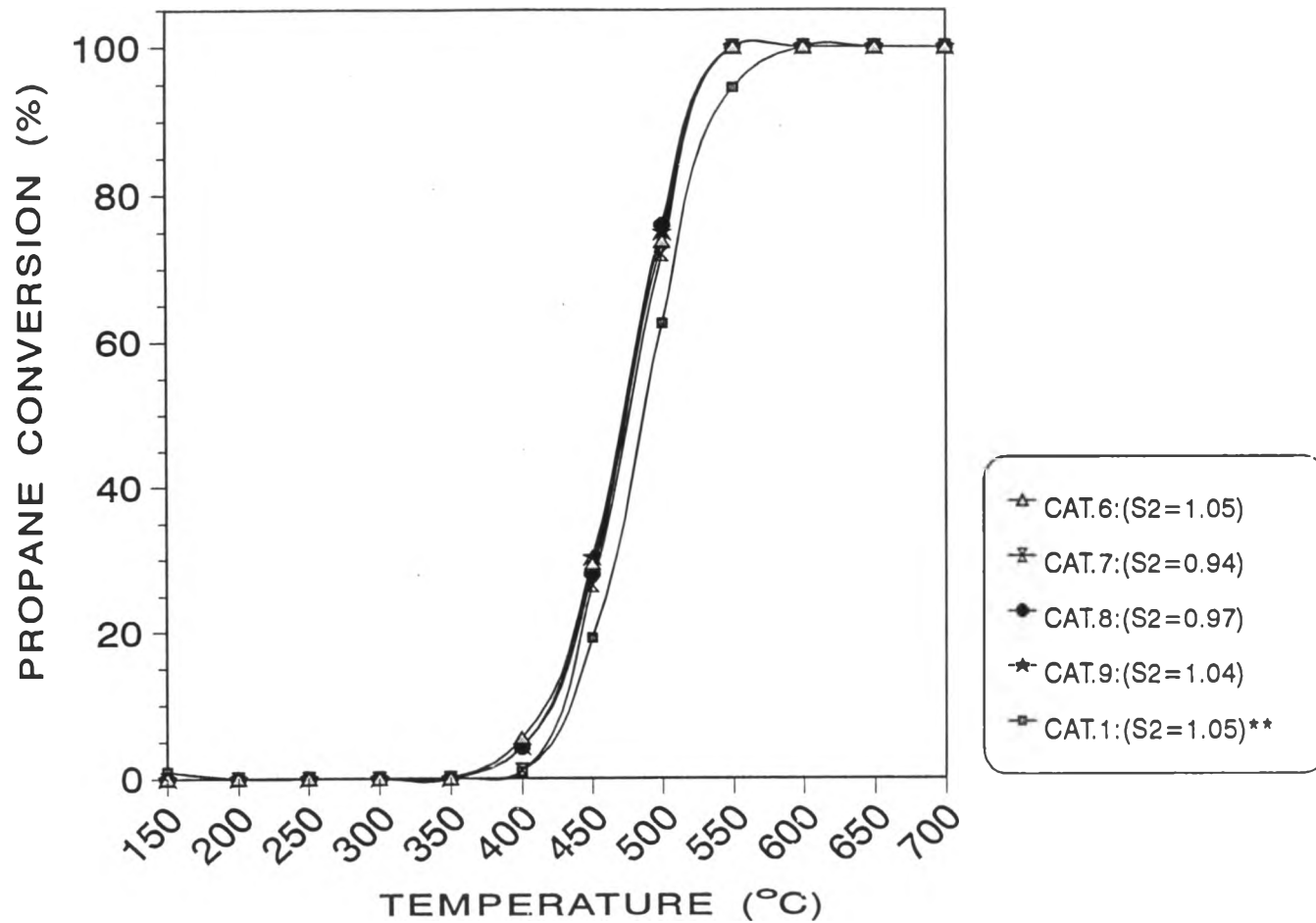


Figure5.13 Effect of various temperature of calcination in reducing atmosphere on Propane conversion in modified three-way catalysts.GHSV=15,000 h<sup>-1</sup> : feed composition at stoichiometric ( S<sub>2</sub> =1.0)

Hence, 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). This phenomena is similarly to the conventional three-way catalyst (Pannee, 1995). And under this treatment, CO chemisorption was decreased and produced the sintering of load metal. The sintering of loading metal cause the decreasing of BET surface area. The BET surface and active site are shown in table 5.5.

Table 5.5 The active site and BET surface area of catalyst calcined in reduce atmosphere (10% $H_2$  /  $N_2$ )

Catalyst	Active site (CO molecule/g.cat.)	BET ( $m^2/g.cat$ )
CAT. 6	$1.93 \times 10^{17}$	239.98
CAT. 7	$1.38 \times 10^{17}$	230.14
CAT. 8	$1.37 \times 10^{17}$	210.61
CAT. 9	$0.91 \times 10^{17}$	163.92

Tauster (1978) reported that a fundamental property of the group VIII noble metal is its ability to chemisorp  $H_2$  and CO, on supports such as  $Al_2O_3$  or  $SiO_2$ . This provide a means of measuring their dispersion. And Chang (1985) found that treatment at high temperature in hydrogen

atmosphere can cause both sintering and SMSI for dispersed metal. Tauster (1981) reported that SMSI phenomenon for supported metallic catalysts comes from a reduction at elevated temperatures 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<sub>2</sub> and CO chemisorption of the supported metals. In addition, the chemisorption properties can explain the physical changes on catalysts, such as agglomeration, encapsulation or incomplete reduction of the supported phase. The chemisorption CO of CAT. 6 to CAT.9 decreases may be a cause of SMSI effect on this catalyst. The BET surface area declines with increasing pretreating temperature, may be evidence of sinter metal plugged on the supported catalyst.

However, the effect of SMSI on NO conversion of modified catalysts leads to the opposite effect from the conventional three-way catalyst which was reported by Pannee (1995). The conventional three-way compound with Ce-Rh-Pt. When metal (group 8B) supported is reduced under hydrogen atmosphere at high temperature, the metal support interaction with the support induce to SMSI phenomenon, and dramatically enhance the activity of NO, CO and propane conversion. In this research has inversely affect only on activity of NO, in spite of CAT.1 which has palladium metal as component in catalyst (metal in group-8B) is pretreated in the same condition (hydrogen atmosphere). Hence, in this experiment studied surface properties of catalyst which is treated under reducing atmosphere at high temperature by using the temperature program reduction technique. (TPR) The provided technique could explain the behavior of absorbed oxygen strength over reduced catalyst surface. The procedure described in chapter IV. The catalysts are performed on this characterization being in table 5.6.

Table 5.6 Catalysts for TPR characteristic.

NAME OF CATALYSTS	CALCINATION CONDITIONS
CAT. D	(Fe/Rh) calcined in air at 500°C
CAT. F	(Pt/Rh) calcined in air at 500°C
CAT. F''	(Pt/Rh) calcined in 10%H <sub>2</sub> /N <sub>2</sub> at 500°C
CAT. 1	(Co/Pd) calcined in air at 500°C
CAT. 9	(Co/Pd) calcined in 10%H <sub>2</sub> /N <sub>2</sub> at 700°C

Figure 5.14 shows TPR profiles of H<sub>2</sub> consumption by various catalysts. It was observed that the maximum peak H<sub>2</sub> consumption of three-way catalyst (CAT.F) is around 220°C while the maximum peak of CAT.1 is around 260°C and 420°C for CAT.D. These results can indicate that the strength of absorbed O<sub>2</sub> on the surface catalyst influences the temperature of maximum H<sub>2</sub> uptake. On the other hand if the strength of absorbed O<sub>2</sub> is stronger, the H<sub>2</sub> uptake is maximum at high temperature. It is reverse result on weak strength of absorbed oxygen.



In heterogeneous reaction system, it has catalysts as active phase. Hence, the reactions could on these active site only. The importance step in heterogeneous reaction, especially on surface catalyst is adsorption and desorption of reactant and product respectively. For redox reaction of three-way catalyst has two-mains reaction (oxidation and reduction). Thereby, the competitive of reactant could be induced. The temperature program reduction technique could be used to interpret the phenomenon on surface. From figure 5.14, it show the order of maximum temperature of H<sub>2</sub> uptake.

$$\text{CAT.F (220}^{\circ}\text{C)} < \text{CAT.1 (260}^{\circ}\text{C)} < \text{CAT. D (420}^{\circ}\text{C)}$$

It could be explained that during redox reaction, there is competitive of NO and oxygen as oxidizing agent to adsorb on active site. From TPR profile of CAT.F uptake H<sub>2</sub> at lowest temperature. It may be a effect of oxide on surface which is removed by H<sub>2</sub> at low temperature, and result in increasing selective of NO on surface. By these phenomena the reduction of NO to N<sub>2</sub> is higher than CAT.1 and CAT.D. ( see figure 5.15) In order to explain the inverse effect of CAT.9 with CAT.F'' which calcined under reducing atmosphere (10% H<sub>2</sub>/N<sub>2</sub>) at 700°C for 7 hrs. TPR profiles are shown in lower than CAT.9 and CAT.F. It corresponds to the results of NO conversion on CAT.F'' , CAT.F, CAT. 1 and CAT.9 , via, the lowest temperature of maximum H<sub>2</sub> consumption, the highest NO reduction. The NO conversion of CAT.F, CAT.F'' , CAT.1 and CAT.9 are shown in figure 5.16.

In summary, the active catalyst for NO conversion should have the TPR prefile in the vicinity of that of the conventional catalyst whose TPR profile was in the range of 200-230°C. That means the active catalyst should have O<sub>2</sub> desorbed at considerably low temperature from which the competitive adsorption of NO to O<sub>2</sub> was favorably affected.

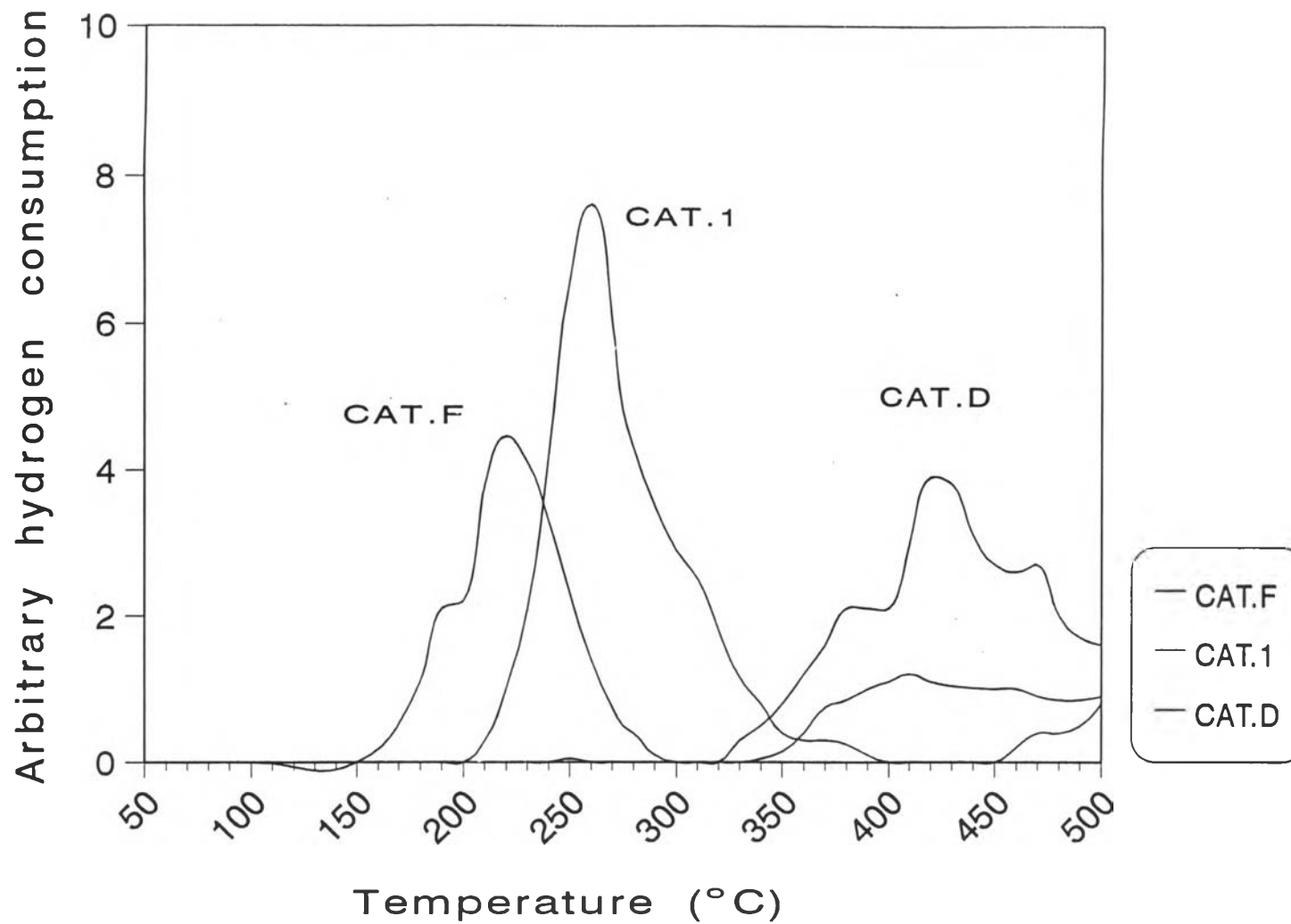


Figure 5.14 The temperature program reduction profiles of H<sub>2</sub> consumption on three-way catalyst and modified three-way catalysts.

# Profile of temperature programme reduction

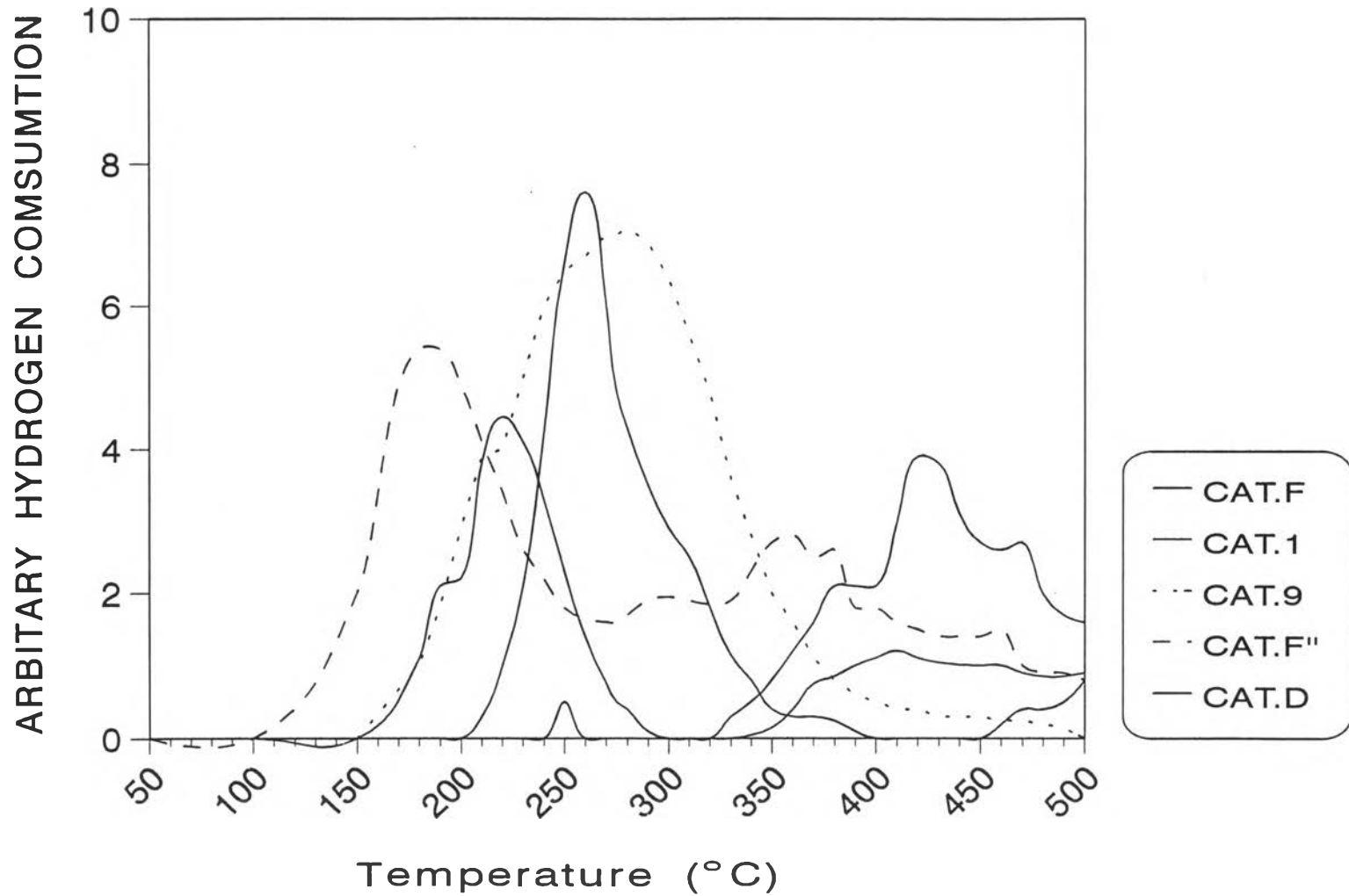


Figure 5.15 The temperature programme reduction profiles of H<sub>2</sub> consumption on three-way catalyst and modified three-way catalysts.

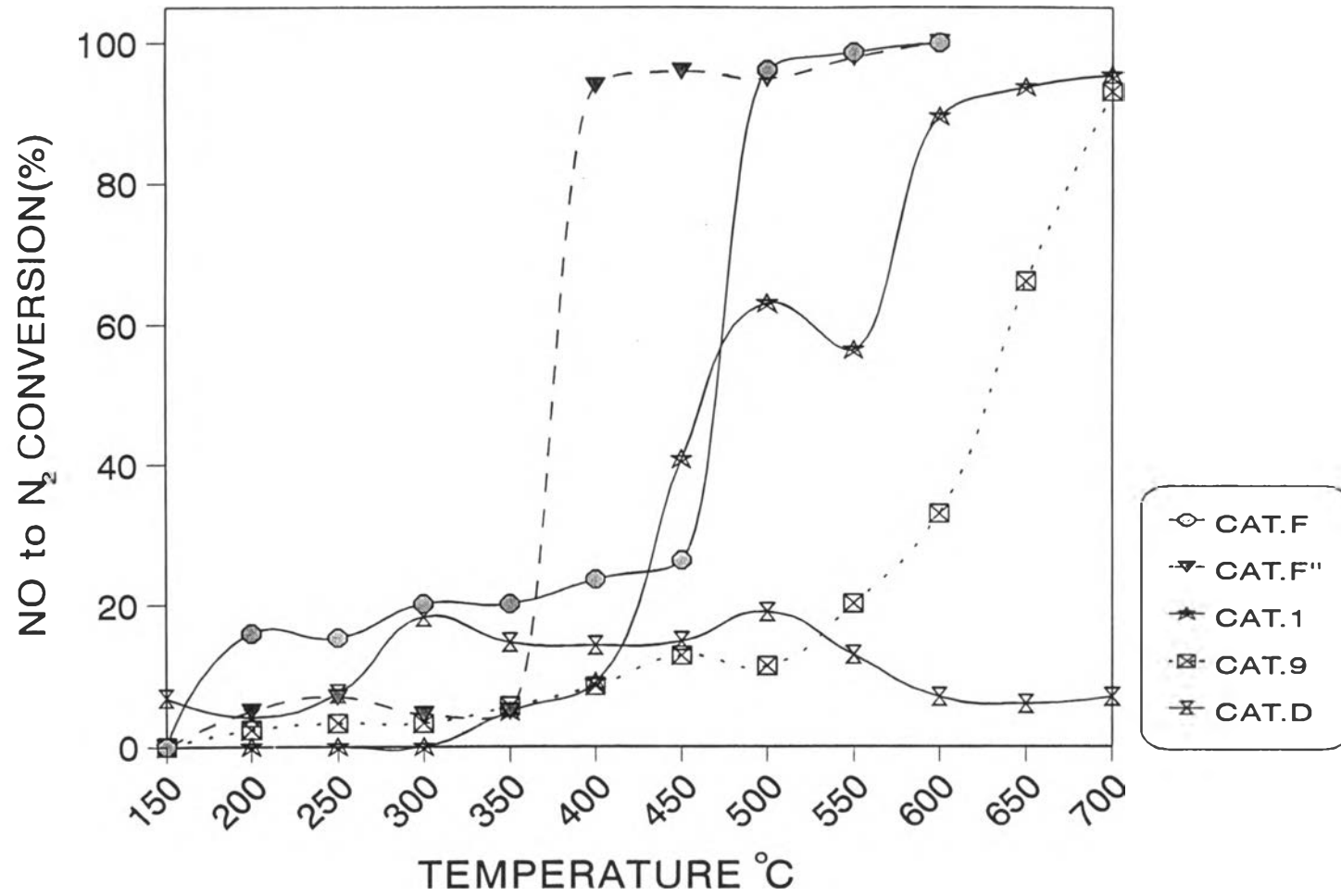


Figure 5.16 Temperature dependence of NO conversion on three-way catalyst (TWC) and modified three-way catalyst (Pd-Co and Fe-Rh).

#### **5.4 Effect of thermal pre-treatment on catalytic activity.**

Refer from previous section (5.3), catalyst prepared by calcination in reducing atmosphere ( $10\%H_2/N_2$ ) can enhance their activity of calcined catalyst under air. In real state operation of drivability, the exhaust component are reducing agent such as carbon monoxide and unburnt hydrocarbon more than oxidizing reagent (oxygen) which may be acting as reducing atmosphere. Hence, it also has possibility that the pretreatment catalyst by it's exhaust, be able to improve the performance the catalytic activity . In this section, the catalyst was prepared by the method similar to CAT.1 but after impregnating palladium metal, said catalyst was pretreated in simulated exhaust as reducing atmosphere. The exhaust gas was simulated at stoichiometric number less than 1.0 ( $S_1 < 1.0$ ). The experiment was divided into two parts for various time of pretreatment (2-10 hrs.) and for various temperature ( $400^{\circ}$ - $700^{\circ}C$ ) at the same condition pretreat: each part describe follows:

##### **5.4.1 Effect of various period time on iso-thermal pre-treatment.**

The catalyst that was studied in these section are described in table 5.7. The NO conversion depend on pretreating time are shown in Figure 5.17. The results are presented that effect of holding time for 2 hrs. (CAT.10) can not enough activate catalytic activity. But when the holding time was increased beyond 2 hrs. to 7 hrs. (CAT.11) and 10 hrs. (CAT.12).

Table 5.7 Name and iso-thermal pre-treatment conditions.

NAME	Thermal Pretreatment Condition
CAT. 10	$S_1^{**} = 0.8$ : for 2 hrs. : 400 °C
CAT. 11	$S_1 = 0.8$ : for 7 hrs. : 400 °C
CAT. 12	$S_1 = 0.8$ : for 10 hrs. : 400 °C

Remark :  $S_1^{**}$  is defined to the stoichiometric number in rich condition of simulated exhaust gas for pretreatment catalyst. ( $S_1 < 1.0$ )

It is obvious that conversion at 600 °C have increased to 92% conversion and 95% conversion for CAT.11 and CAT.12 respectively, with respect to CAT. 10 and average of both catalysts about 95% conversion from 600-700 °C. Although increasing of conversion is different, the light-off temperature is slightly different in each other. For CO conversion is shown in figure 5.18, the activity of CO conversion increases with increasing holding time. It is observed that the profile CO conversion of CAT.12 overlap on profile of CAT.1 in the range 300°C to 700°C. In addition, these pretreatment can enhance propane conversion. When the holding time increases, the temperature of maximum conversion (100%) shift downs. In figure 5.19 shows, the maximum propane conversion was obvious decreased from 650°C to 600°C and 550°C for catalyst CAT.11 and CAT.12 respectively. And the light-off temperature are not different, that is about 470°C.

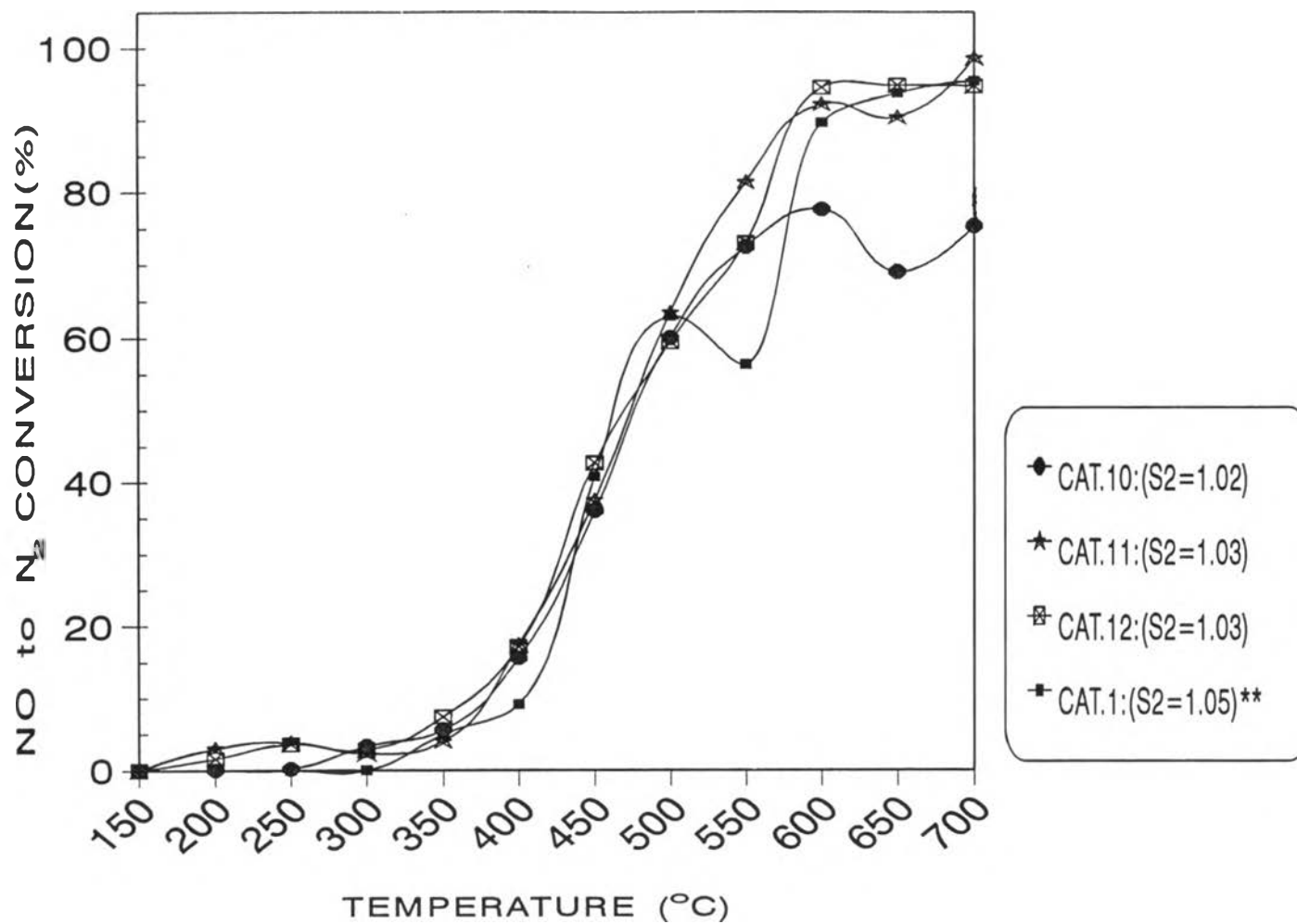


Figure 5.17 Effect of time on iso-thermal pretreatment for NO conversion of modified three-way catalysts. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub> =1.0)

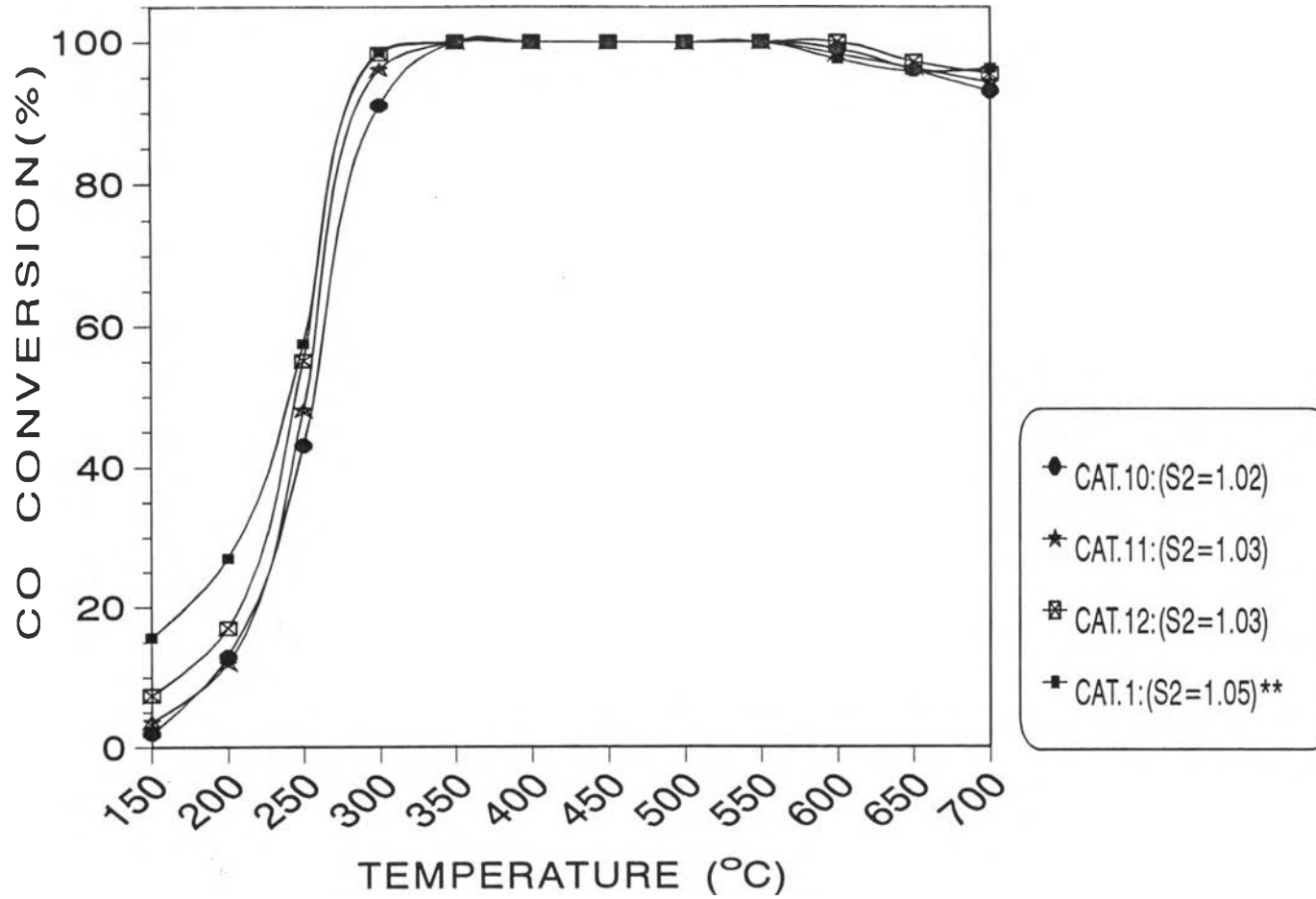


Figure 5.18 Effect of time on iso-thermal pretreatment for CO

conversion of modified three-way catalysts. GHSV = 15,000 h<sup>-1</sup>

feed composition at stoichiometric (S<sub>2</sub> = 1.0)



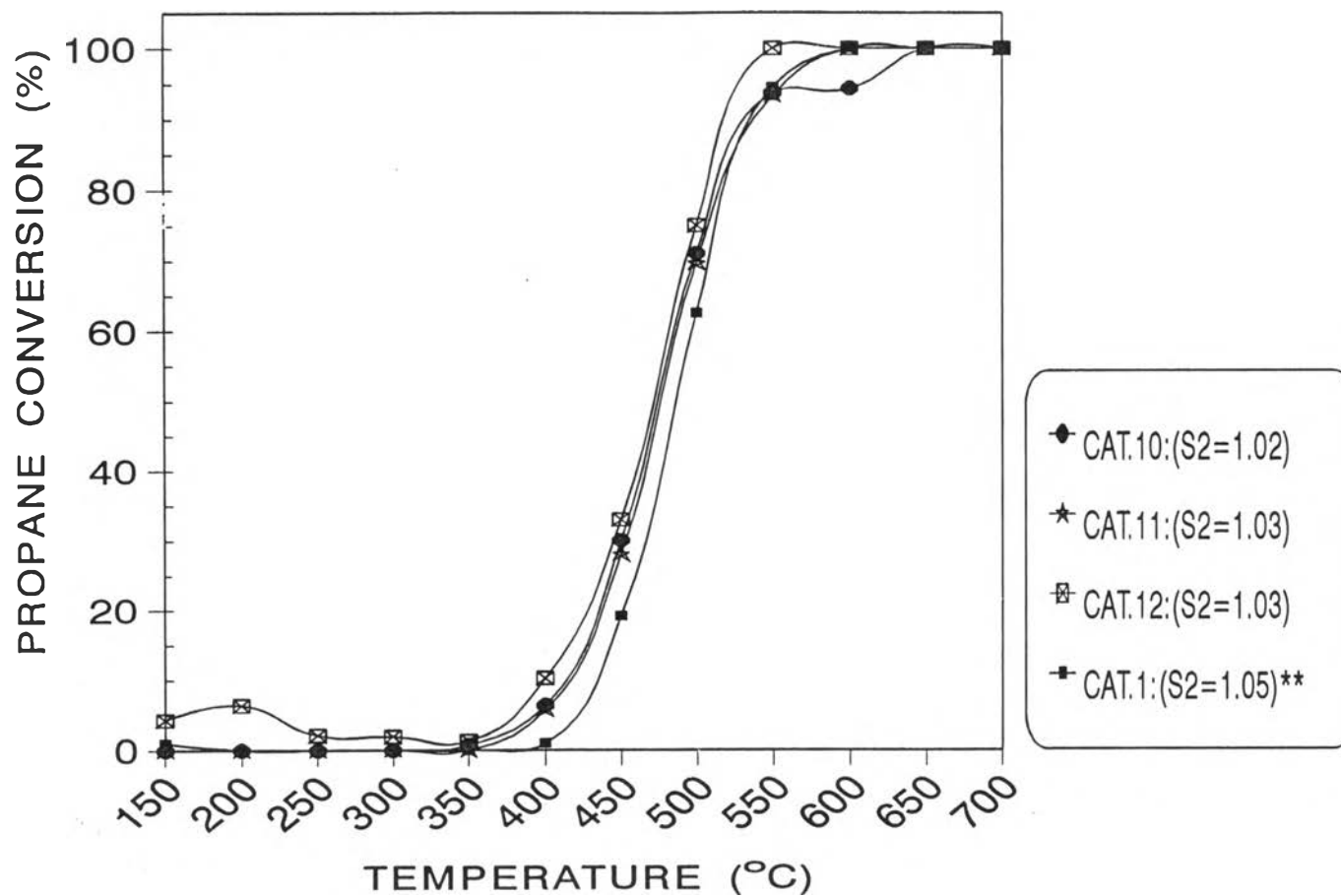


Figure 5.19 Effect of time on iso-thermal pretreatment for Propane conversion of modified three-way catalysts. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

From these result, it can be summarized that the best condition for pretreated catalyst is pretreatment in reducing gases at 400°C for 7 hrs. Mainly because of efficiency of CAT.11 as well as CAT.12, hence the 7 hours. is very suitable. Furthermore, it is should be better to examine the effect of pretreating temperature on the catalyst activity.

#### 5.4.2 Effect of various temperature on thermal pre-treatment.

For the pre-treatment method which was presented by Pannee,1995, the modified of conventional three-way catalyst can exhibit the higher efficiency by pre-treatment in rich condition at high temperature about 700°C.

For the optimum thermal treatment, the modified three-way catalysts were studied by vary temperature with the method of pre-treatment in the rich condition.

Table 5.8 Name and pre-treatment conditions

NAME	PRETREATMENT CONDITION
CAT. 11	$S_1 = 0.8 : 400\text{ }^\circ\text{C} : 7\text{ hrs.}$
CAT. 13	$S_1 = 0.8 : 500\text{ }^\circ\text{C} : 7\text{ hrs.}$
CAT. 14	$S_1 = 0.8 : 600\text{ }^\circ\text{C} : 7\text{ hrs.}$
CAT. 15	$S_1 = 0.8 : 700\text{ }^\circ\text{C} : 7\text{ hrs.}$

Remark :  $S_1^{**}$  is defined to the stoichiometric number in rich condition of simulated exhaust gas for pretreatment catalyst. ( $S_1 < 1.0$ )

The results are shown in Figure 5.20 for NO conversion that when the temperature for pretreatment was increased from 400° to 500°, 600°, 700°C. The light-off temperature was increased to 470°, 560°, 650° C for CAT.11, CAT. 13, CAT.14 and CAT.15, respectively. While, this pretreatment present the contrast influence on CO conversion. Figure 5.21 shows the advantage of pretreatment in high temperature for oxidation CO. The result show that the catalyst in higher temperature pretreatment are much more active than lower temperature. The CO conversion attains 100% at only 250°C when the catalyst were pretreated at 600°C and 700°C. While the pretreated temperature decrease to 500°C and 400°C the maximum temperature skip to 300°C and 350°C respectively. And conversion of CO fell down when reaction temperature over 500°C. The result of propane conversion are shown in Figure 5.22. It shows that thermal pretreatment in rich condition can improve the activity of catalyst if the temperature pretreatment is higher than 400°C.

In summary, it showed that the thermal pretreatment for fresh catalyst can improve the activity of catalyst on conversion of three pollutants. But each of conversion have different results by influence of pretreating temperature. Comparison to CAT.1 if the pretreatment performs at 400°C , the activity of NO conversion is improved while pretreat in high temperature beyond 400°C the calalysts activity are much more suppressed than the CAT.1 (calcining in air atmosphere). On contradiction, when the catalysts are treated in high temperature, the activity of CO conversion are enlarged according to level of pretreating temperature. And this effect is presented

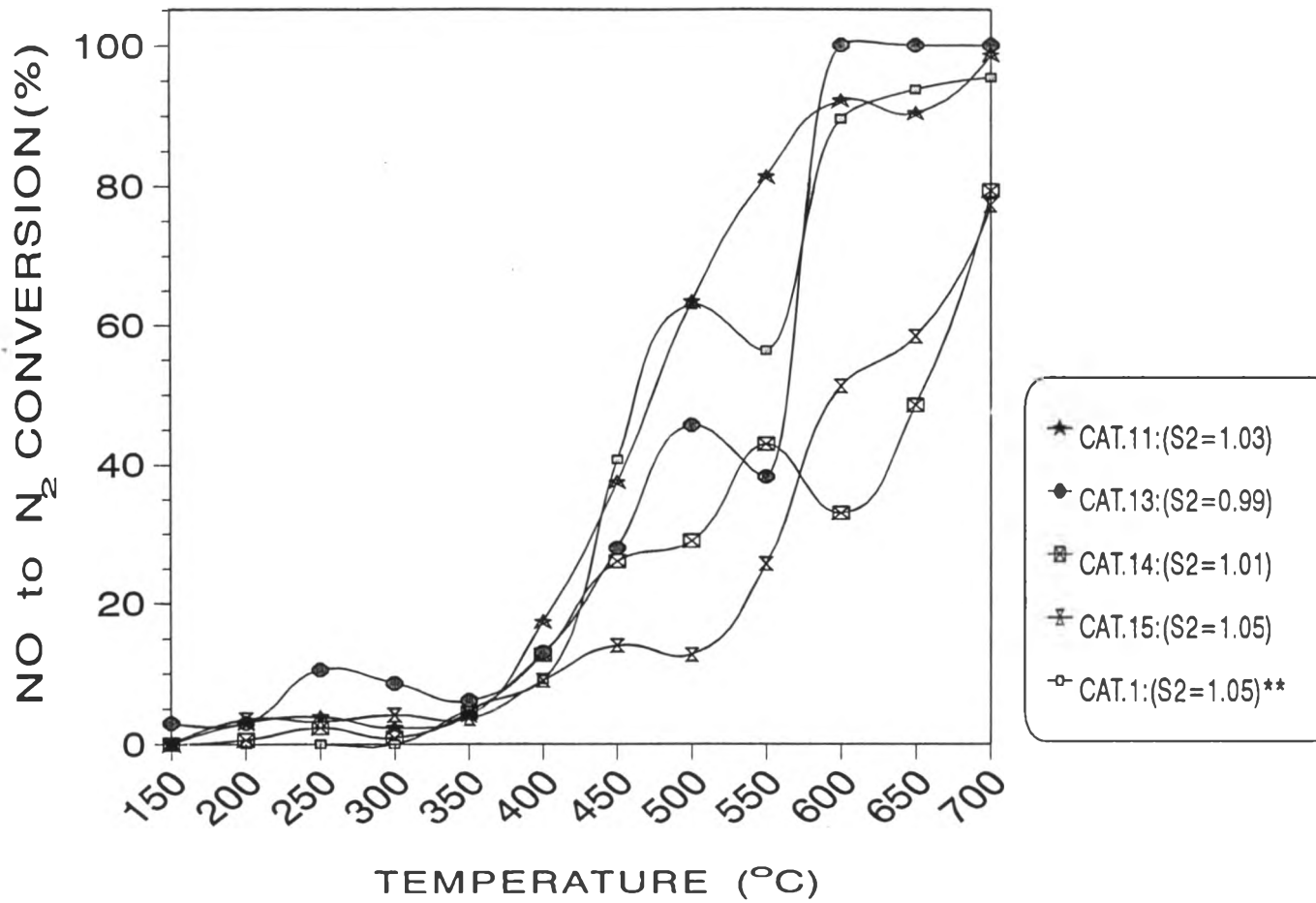


Figure 5.20 Effect of various temperature for thermal pretreatment on NO conversion of modified three-way catalysts. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

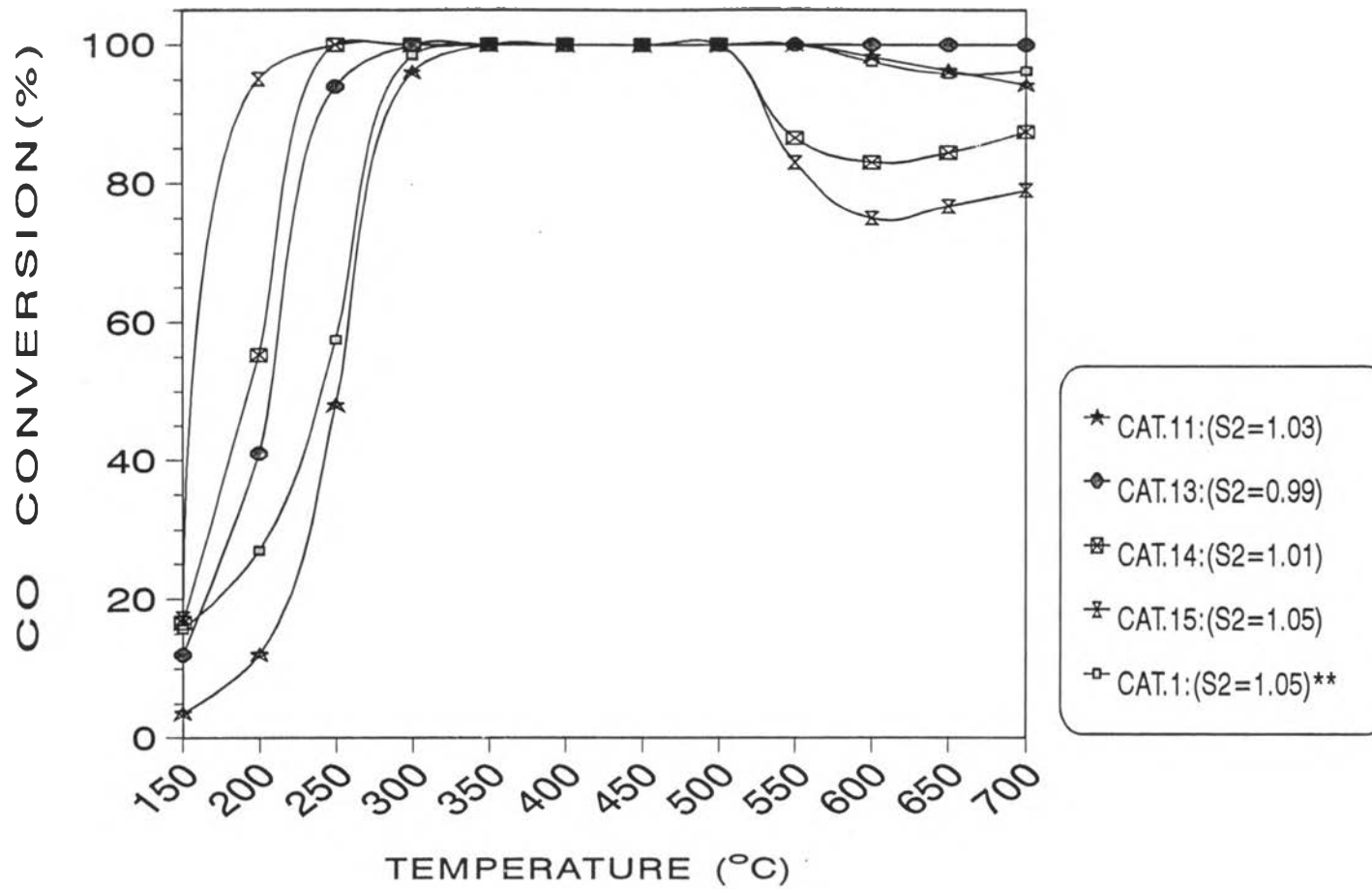


Figure 5.21 Effect of various temperature for thermal pretreatment on CO conversion of modified three-way catalysts. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub> = 1.0)

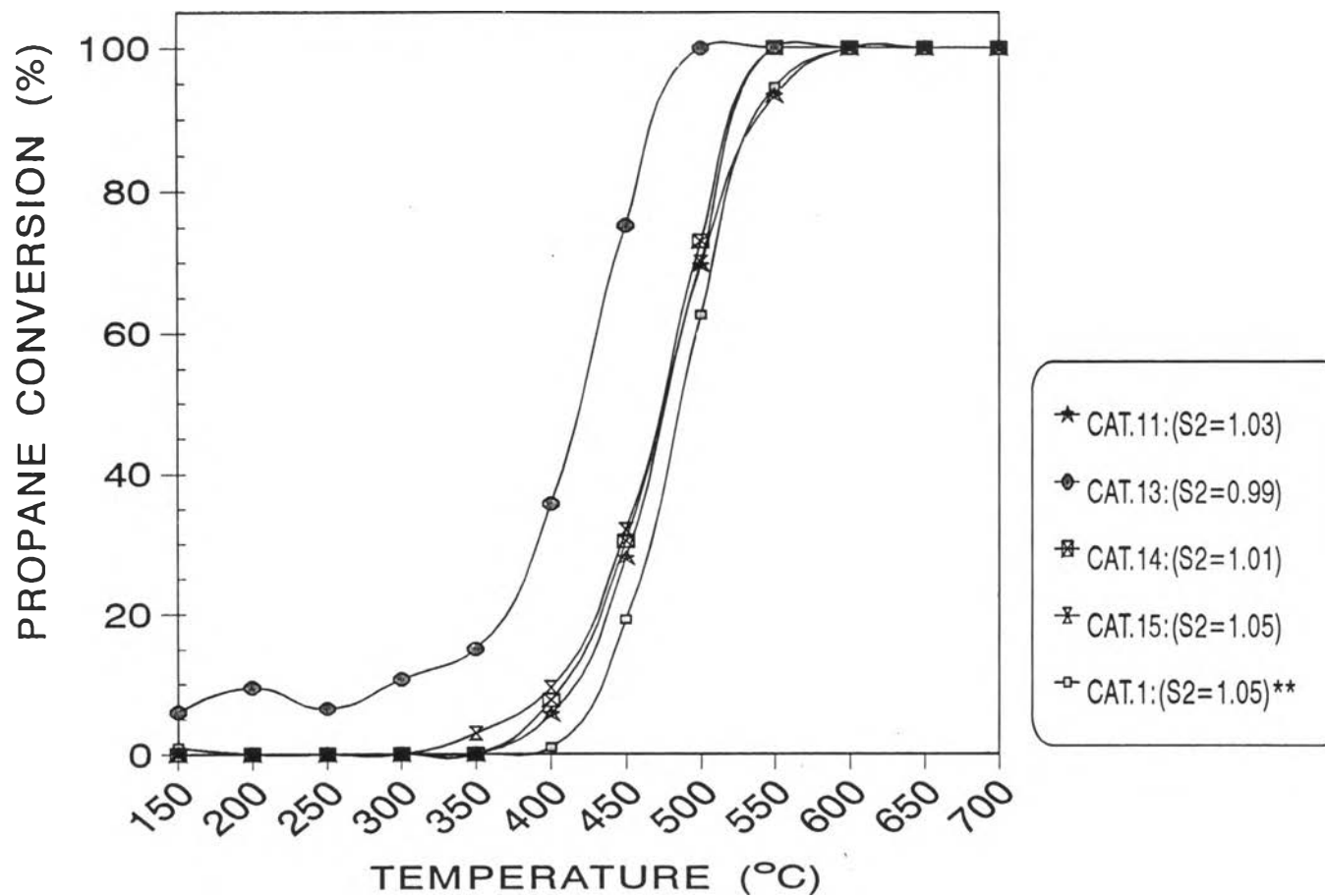


Figure 5.22 Effect of various temperature for thermal pretreatment on

Propane conversion of modified three-way catalysts.

GHSV=15,000 h<sup>-1</sup>, feed composition at stoichiometric (S<sub>2</sub>=1.0)

on propane. The light-off temperature that indicated activity of catalyst are decreased while the pretreating temperature increased.

From the results of parts 5.3 to 5.4 which the catalysts were prepared by calcining in 10% $H_2/N_2$  and thermal pretreatment in simulated rich mixture of exhaust gas. The operation associate with various period of calcination time, vary temperature and vary simulated exhaust gas. We would consider the suitable condition for modified catalysts. From the results of each parts, the best catalyst was taken to compare. There are four catalysts which are shown in table 5.9.

Table 5.9 Show various pre-treating condition catalysts.

CATALYSTS	PRE-TREATED CONDITIONS
CAT. 1	air atmosphere , 500°C , 4 hrs.
CAT. 6	10% $H_2/N_2$ , 400°C , 7 hrs.
CAT.11	$S_1 = 0.80$ , 400°C , 7 hrs.
CAT.16	$S_1 = 1.05$ , 400°C , 7 hrs.

Remark :  $S_1$  is the mixture of exhaust gases at stoichiometric composition for pretreat catalysts.

Figure 5.23 as show the NO conversion of the catalyst which pretreated from various conditions. All condition performed on 400 °C. The result of NO conversion was devided into 2 ranges that is between 150-500°C, there is no different on activity of catalyst. But temperature in the range

between 500-700 °C, it can be clearly observe that the catalysts which prepared from calcining in reducing atmosphere more enhance in the activity than calcining in oxidizing atmosphere. Especially, at temperature 550°C, CAT.6 attain NO conversion (90%) higher than CAT.11, there is 80% NO conversion. And both catalyst has activity higher than CAT.1 and CAT.16 It could be indicated that it is a cause from pretreated catalyst in reducing atmosphere. The CO conversion is shown in figure 5.24, there is only CAT.9 which has high activity on range 150-300°C, but when temperature above 500°C , there is inverse results in first range, that is conversion slow downs to 85% at 700°C while other catalyst's conversion slightly decreases, especially CAT.16. It may be that the metal supported catalyst in metal form has been stable lesser than oxide form. The effect of pretreating condition on propane conversion are shown in figure 5.25. There are slightly different in various catalyst which was pretreated in reducing atmosphere ( both of H<sub>2</sub> and rich condition). However, the catalyst which was pretreated in reducing agent atmosphere (CAT.9, CAT.11) and stoichiometric condition (CAT.15) slightly enhance CAT.1(calcining in air atmosphere) from 400-550°C when rise up over 400°C there is no different on propane conversion.

From the result, it can be concluded that in each conditions of pretreated the modified three-way catalyst lead to different effect on NO, CO and propane conversion. In this studied, the light of temperature index is used to be a criterion for comparable activity of catalysts.



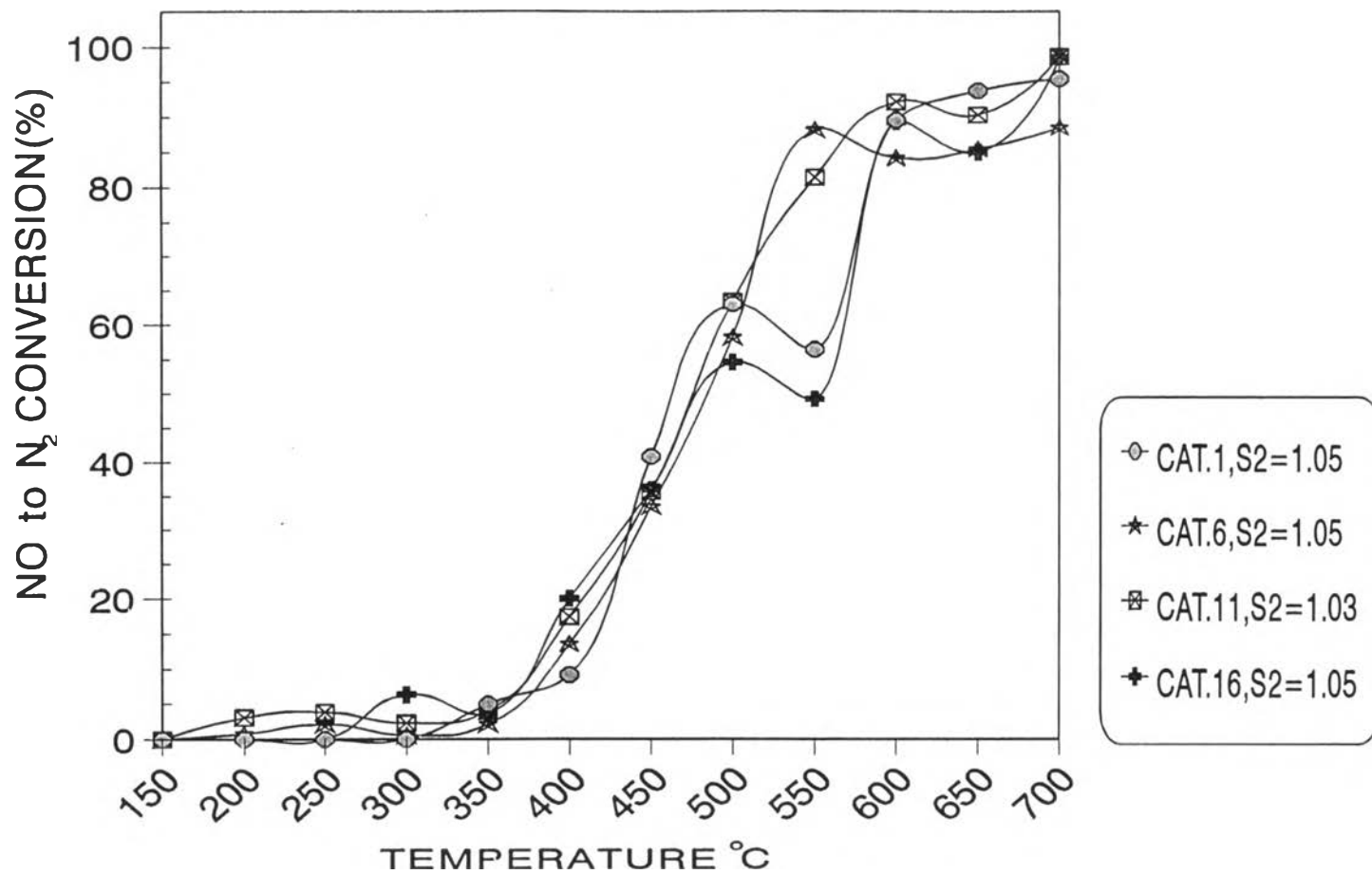


Figure 5.23 Effect of the pretreatment condition on modified three-way catalysts for NO conversion. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

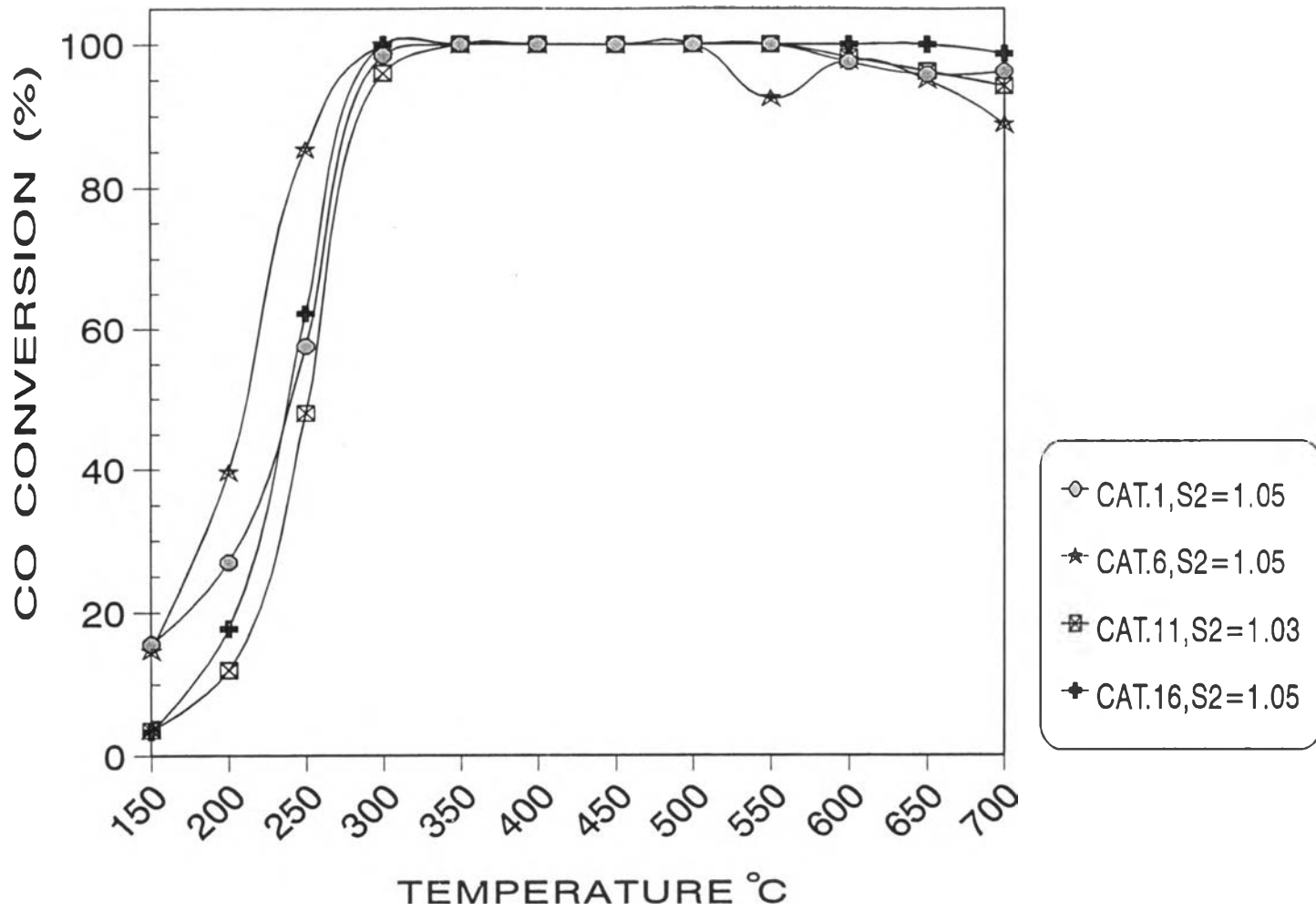


Figure 5.24 Effect of the pretreatment condition on modified three-way catalysts for CO conversion. GHSV=15,000 h<sup>-1</sup>  
 feed composition at stoichiometric (S<sub>2</sub>=1.0)

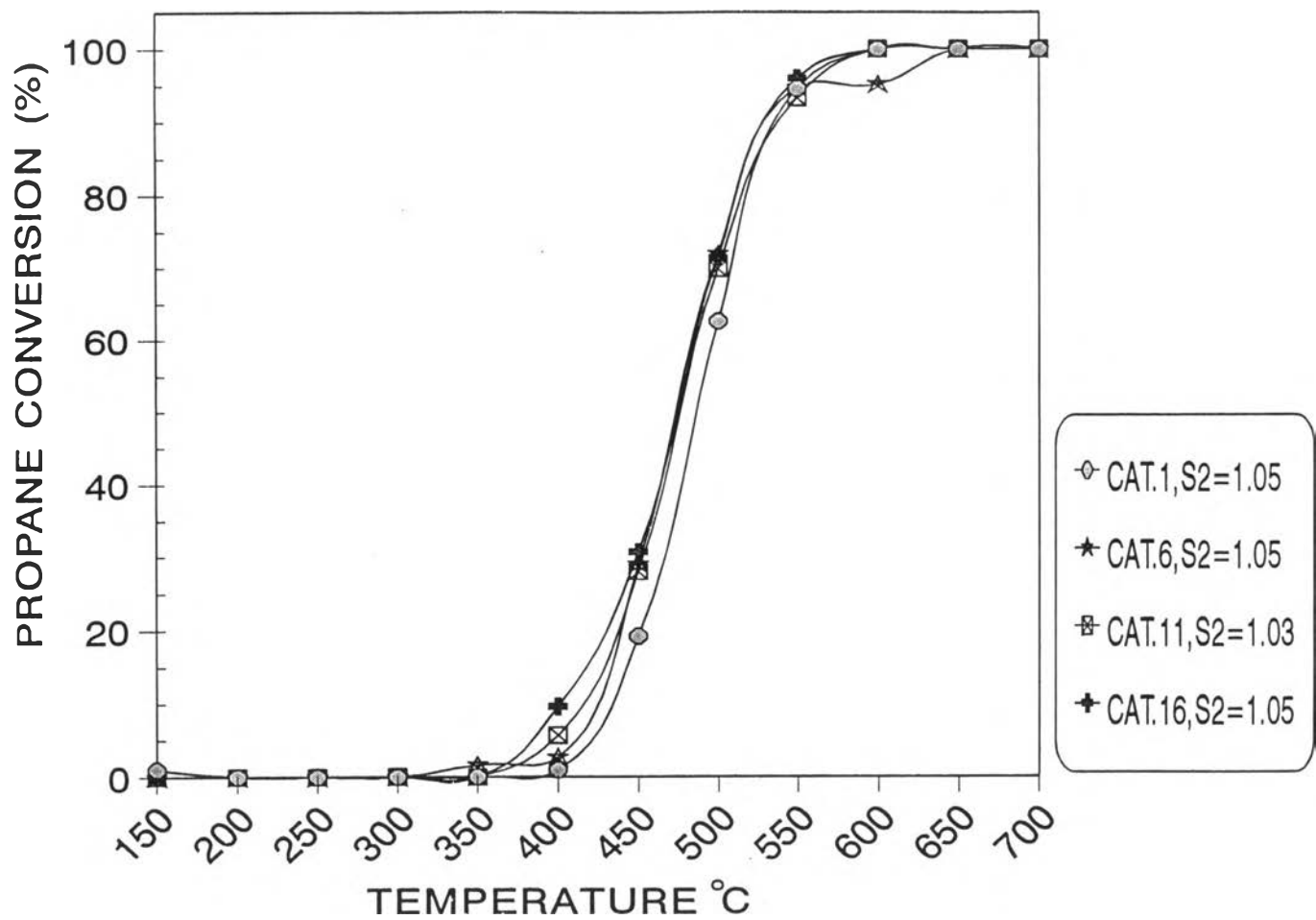


Figure 5.25 Effect of the pretreatment condition on modified three-way catalysts for propane conversion. GHSV=15,000 h<sup>-1</sup> feed composition at stoichiometric (S<sub>2</sub>=1.0)

Table 5.10 Light-off temperature of pre-treated catalysts.

CATALYSTS	LIGHT-OFF TEMPERATURE (°C)		
	%NO CONV.	%CO CONV.	%C <sub>3</sub> H <sub>8</sub> CONV.
CAT.1	460	240	475
CAT.6	485	210	475
CAT.11	470	250	475
CAT.16	485	235	475

From data in table 5.10, CAT.1 is lowest light-off temperature on NO conversion, but highest activity of CO conversion is CAT.6. However, the advantage of pre-treated catalyst in reducing atmosphere is interesting for actual operating of drivability.

The active site and BET surface area are shown in table 5.11.

Form data in table, the active site and BET surface area trend to decrease with increasing pretreating temperature. In assumption that the rich condition ( $S_1 = 0.8$ ) in exhaust gases is similar to reducing condition of hydrogen atmosphere. Then, it can be effect of SMSI on metallic supported catalyst.

Table 5.11 The active and BET surface area of catalyst pretreated in feed mixture (rich mixture :  $S_1 = 0.8$  ) atmosphere.

Catalyst	Active site (CO molecule/g.cat.)	BET (m <sup>2</sup> /g.cat)
CAT. 11	$1.96 \times 10^{17}$	187.97
CAT. 12	$1.70 \times 10^{17}$	192.89
CAT. 13	$2.36 \times 10^{17}$	192.74
CAT. 14	$0.42 \times 10^{17}$	177.39
CAT. 15**	$2.59 \times 10^{17}$	190.34

Remark : \*\* is catalyst which pre-treated at stoichiometric composition ( $S_1 = 1.05$ ).

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

In this section was investigated effect of oxygen content on the three-way catalyst performance. This experiment examined at 700 °C and vary O<sub>2</sub> - content for various air/fuel ratio.

Air/fuel is defined in term of stoichiometric number: " S ". The conversion of NO , CO and propane is plotted as function of stoichiometric number (S) are shown in figure 5.26.

CAT.1 and CAT.6 were proposed in order to compare the performance between calcining in air (CAT.1) and reducing atmosphere (CAT.6). The results show that under condition in slight oxidizing environment ( $S > 1 \pm 0.05$ ) the NO conversion level is sharply down while propane and CO conversion level are very high. In reducing condition ( $S < 1 \pm 0.05$ ) the NO conversion is relatively high, while the propane and CO conversion

decrease with decreasing  $S$ . Between CAT.1 and CAT.6 it is found that the performance of CAT.1 is higher than CAT.6 on NO, CO and propane conversion. It could not indicate in term of "window" on CAT.6 Because NO component is very sensitive with  $O_2$ -content around stoichiometric condition ( $S=1 \pm 0.05$ ). For CAT.1, the window could be defined as  $1 \pm 0.03$  on NO conversion. However, the CO and propane component could be exhibited correspond to the conventional three-way catalyst (noble-metal catalyst). (Pannee,1995) The window is defined by the conversion which achieve 80 % conversion. (Wei,1975)

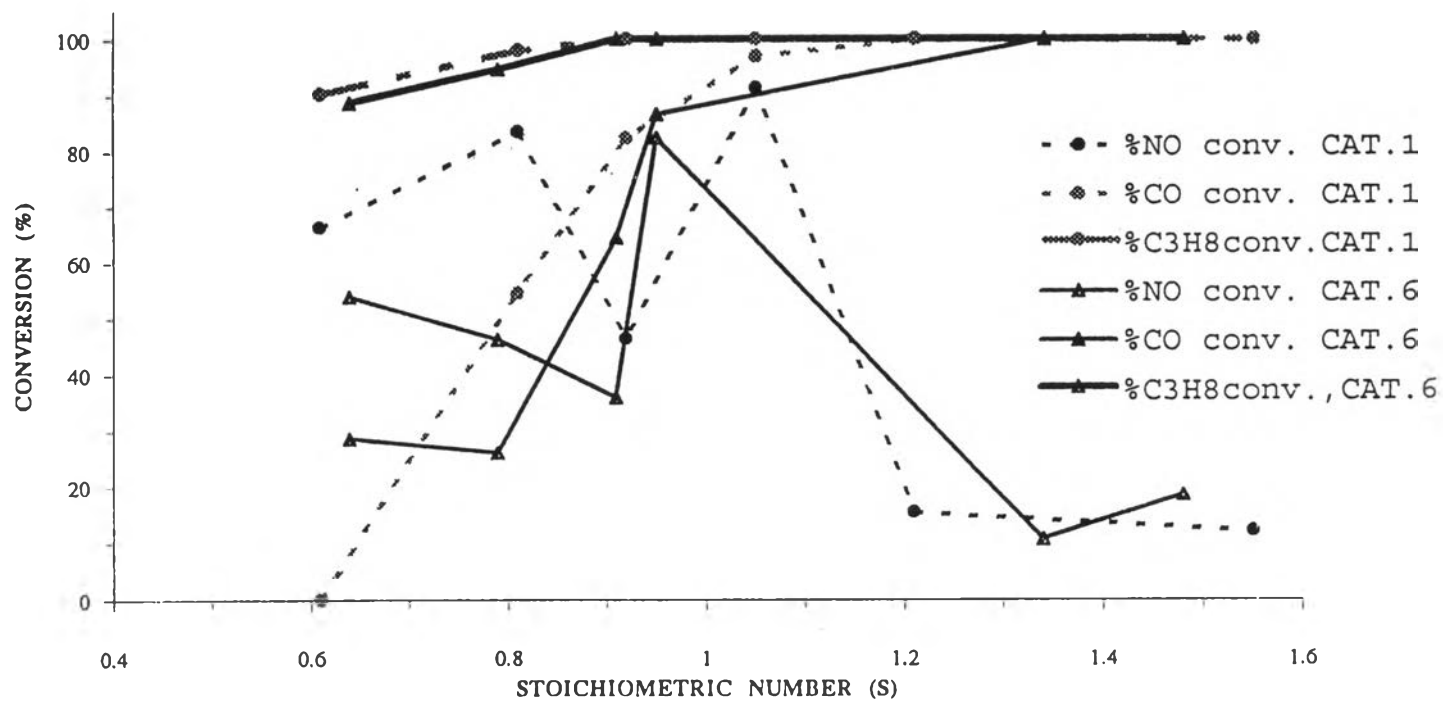


Figure 5.26 Effect of the air/fuel ratio on NO, CO and Propane conversion of CAT.1 and CAT.6 at 700°C and GHSV=15,000 h<sup>-1</sup>