CHAPTER V

RESULTS AND DISCUSSIONS

The main feature of this research was to develop a copper catalyst used for carbon monoxide oxidation reaction. Majority of the work had been relied on the data of the previous work of Catalysis Research Laboratory, Department of Chemical Engineering, Chulalongkorn University [51]. The results and discussions were categorized into three parts as follows.

5.1 Effect of Calcination Temperature on the Activity of Catalysts: In this part, the relationship between SMSI state and calcination temperature in the preparatory step of copper catalyst was studied and discussed in detail.

5.2 Effect of Platinum on Copper Catalysts: The variation of platinum loading, second metal incorporation in copper catalyst, were made to find out a suitable amount that give the highest activity for CO oxidation reaction and then the calcination period was also varied for that suitable platinum-copper catalyst. Several platinum-copper catalysts were characterized by various methods in order to discuss the results.

5.3 Metal-Metal Interaction in Platinum-Copper Catalysts: In this part, metal-metal interaction in platinum-copper catalyst was observed by the effect of copper on CO adsorption of platinum.

5.1 Effect of Calcination Temperature on the Activity of Copper Catalysts

The first experiment of this research was to study the effect of calcination temperature on the activity of copper catalysts for CO oxidation reaction. Huang et al. [5] found that high temperature calcination in a reducing atmosphere produced a sintered copper surface but induced a strong metal-support interaction (SMSI) which caused a large increase in activity. Foger [52] reported that a general feature of metals in the SMSI state was an enhanced activity for reactions involving carbon monoxide, such as Fischer-Tropsch synthesis, methanation and the CO-NO reaction. Therefore, a series of copper catalysts, as shown in Table 5.1, was prepared and characterized in order to prove the proposition of Huang.

From Table 5.1, four catalysts, name as CAT.3 to CAT.6, were studied. In this group of catalysts, both calcination atmosphere and period of calcination were fixed but the calcination temperature was varied from 500 °C to 800 °C. All of the prepared copper catalysts were tested for its activity on CO oxidation reaction. After the activity test, all copper catalysts were characterized by CO adsorption capacity measurements, temperature-programmed desorption of CO_2, specific electrical conductivity measurements, metal active sites measurements, and BET surface area measurements.

Figure 5.1 shows the conversion of CO as a function of reaction temperature. It was observed that the activity of catalyst was increased as a function of the calcination temperature. This indicated that high temperature calcination in a reducing atmosphere cause a beneficial effect which is in agreement with the

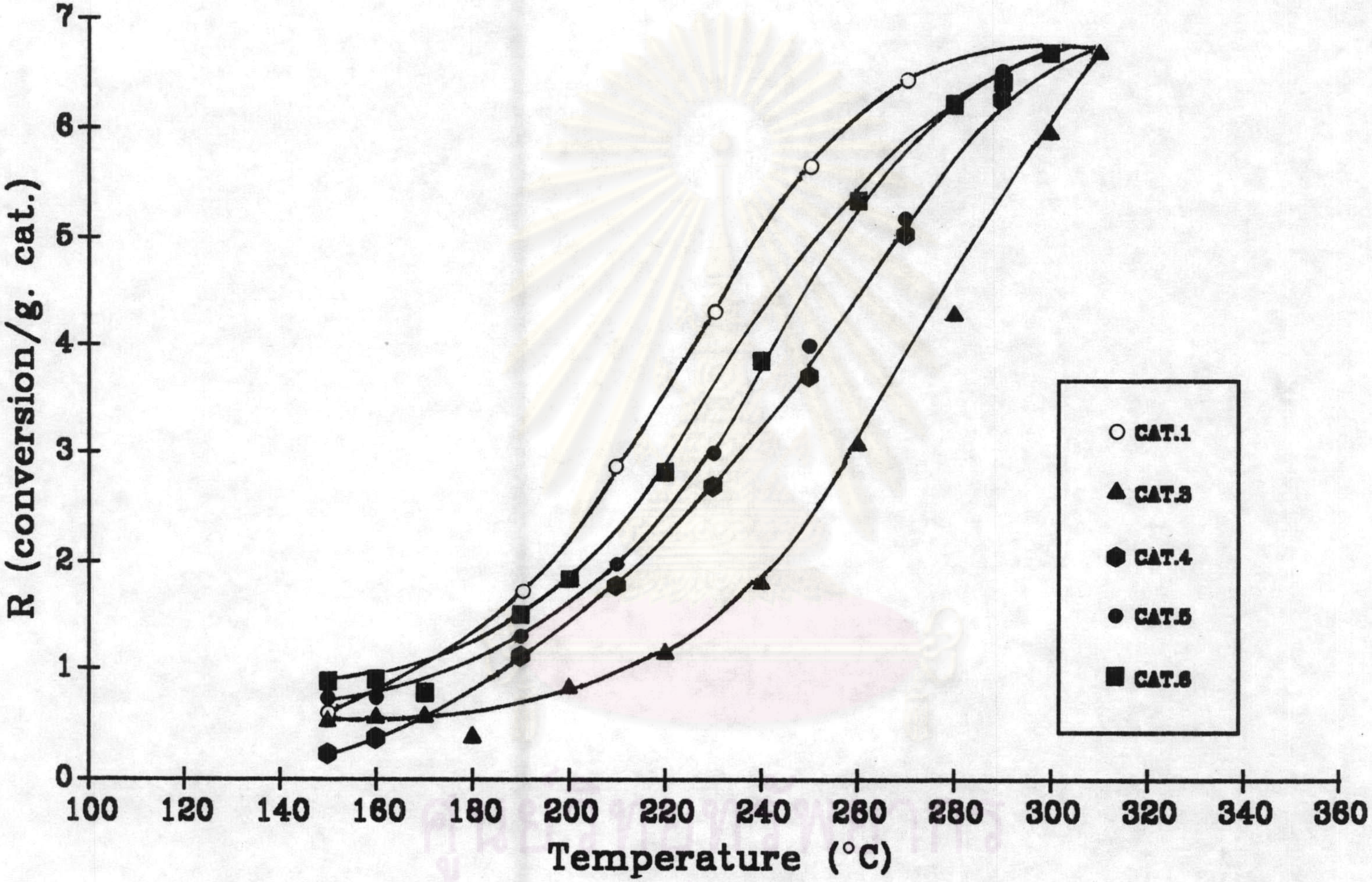

Figure 5.1 Activity in CO oxidation of copper catalysts calcined at various temperatures: CAT.1 was the copper catalyst prepared by Huang method [5].; CAT.3, CAT.4, CAT.5, and CAT.6 were the copper catalysts calcined at 500˚, 600˚, 700˚,and 800˚C, respectively.

Table 5.1 CO Adsorption Capacity, CO_2 Adsorption Capacity, CO_2 Adsorbable Strength, and Specific Electrical Conductivity Data of Copper Catalysts

Catalysts (ref. to Table 4.1)	CO Adsorption Capacity (μmol/g.cat.)	CO_2 Adsorption Capacity (μmol/g.cat.)	$t_{d,max}$* (°C)	BET (m^2/g.cat)	Specific Electrical Conductivity ($ohm^{-1}cm^{-1}$)
CAT.1	29.36	41.03	100	108.96	1.79×10^{-6}
CAT.2	152.45	153.26	150	258.37	0.71×10^{-6}
CAT.3	60.74	72.40	130	246.87	1.21×10^{-6}
CAT.4	48.27	57.92	120	193.37	1.46×10^{-6}
CAT.5	32.18	51.48	120	181.41	1.63×10^{-6}
CAT.6	19.25	43.84	120	146.61	1.92×10^{-6}
CAT.7	41.90	60.30	140	188.52	1.28×10^{-6}

* $t_{d,max}$ is the CO_2 adsorbable strength which was expressed by the temperature at the maximum CO_2 desorption.

findings of Huang et al. [5].

Table 5.1 shows the capacities of catalysts for CO, CO_2 adsorptions and CO_2 adsorbable strength expressed by the temperature giving the maximum desorption of CO_2. In addition, the values of specific electrical conductivity were also included in this table. From the table, it was observed that the increase in calcination temperature has resulted in the decrease in the adsorption capacity of CO while the change of specific electrical conductivity undergone

Table 5.2 Amount of Reacted N_2O Data of Copper Catalysts

Catalysts (ref. to Table 4.1)	Amount of reacted N_2O (molecules/g.cat.)
CAT.1	0.86×10^{19}
CAT.2	3.07×10^{19}
CAT.3	1.52×10^{19}
CAT.4	1.20×10^{19}
CAT.5	0.95×10^{19}
CAT.6	0.55×10^{19}
CAT.7	0.44×10^{19}

in the opposite direction to the CO adsorption capacity. This indicates that the SMSI state may be induced [53,49] and is in agreement with Huang et al. [24] who proposed that the SMSI effect was stronger for higher calcination temperatures. Moreover, in this research, it was also found that the tendency for CO_2 adsorption capacity was similar to the CO adsorption capacity. The evidence that confirms the type of CO or CO_2 adsorption, whether it is a physical adsorption, is the data of BET surface area as shown in Table 5.1. From the physical properties data of the alumina as shown in Appendix B, surface area of alumina is about 350 m^2/g but BET surface area, as shown in Table 5.1, of the catalysts was in the range from 108 to 260 m^2/g. This result could be explain that the pores of support to be pluged by the loaded metal (copper). Therefore, the surface area of catalyst was lower than the surface area of alumina. BET data can confirm in the type of CO, CO_2

adsorption because N_2, used in BET method, is adsorbed on the sample by the physical adsorption [54]. If the amount of CO, CO_2 adsorbed on the catalyst is in consistent with BET data, it can conclude that CO, CO_2 adsorbed on the catalyst by physical adsorption. It was obviously seen from Table 5.1 that BET data was not in consistent with the data of the amount of CO, CO_2 adsorbed on the catalysts such as when compare CAT.1 to CAT.6. Therefore, the type of adsorption of CO, CO_2 was not a physical adsorption.

Figure 5.2 shows the TPD profiles of CO_2 on copper catalysts calcined under reducing atmosphere at temperature of 500°, 600°, 700° and 800 °C for 3 hours. It was observed that, the CO_2 adsorbable strength of copper catalysts were around 120 °C when the calcination temperature was more than 600 °C. At the calcination temperature of 500 °C, CO_2 adsorbable strength was about 130 °C. These results corresponded with the activity test of catalysts as discussed previously. As shown in figure 5.1, CAT.4, CAT.5, and CAT.6 had a little difference in activity except for CAT.3. A difference in activity between the three former catalysts and CAT.3 were caused by the CO_2 adsorbable strength whereas a little difference in activities among the three former catalysts might be resulted from the amount of CO_2 adsorption on them.

Table 5.2 shows the amount of copper active sites which was measured by the reaction with nitrous oxide. It was seen that the amount of copper active sites was decreased as the calcination temperature was increased. This was presumably caused by the sintering of copper atoms [5,26]. In other words, the reductive treatment at higher temperature produces more sintered copper atoms.

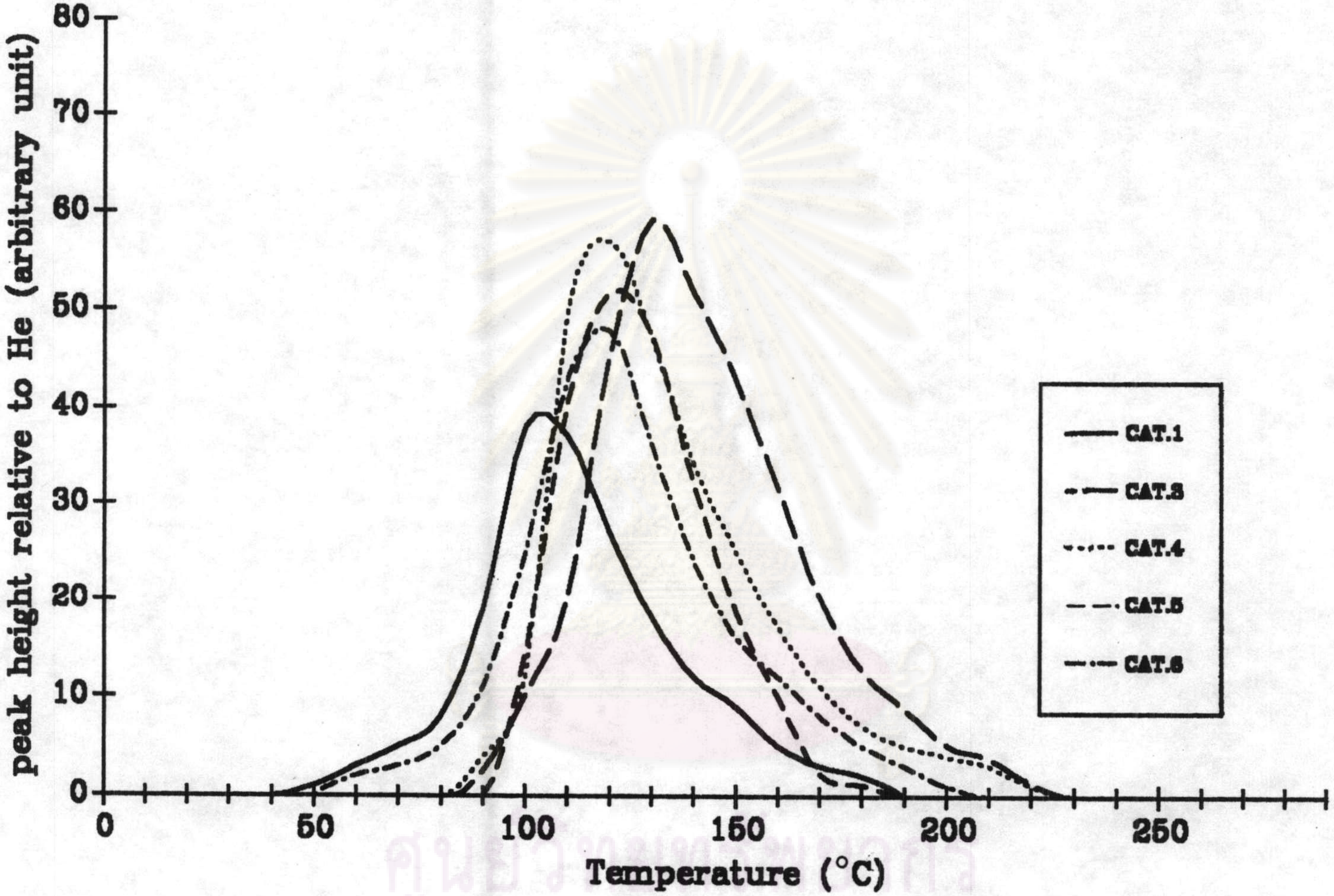

Figure 5.2 The temperature-programmed desorption profiles of CO_2 on copper catalysts: CAT.1 was the copper catalyst prepared by Huang method [5].; CAT.3, CAT.4, CAT.5, and CAT.6 were the copper catalysts calcined at 500°, 600°, 700°, and 800°C, respectively.

Table 5.3 Copper contents of various copper catalysts and platinum contents of platinum incorporated copper catalyst which were measured by AA and ICPS methods

Catalysts sample (ref. to Table 4.1 and 4.2)	Platinum contents (wt. %)	Copper contents (wt. %)
CAT.1	-	7.48
CAT.3	-	7.56
CAT.4	-	7.45
CAT.5	-	7.52
CAT.6	-	7.46
CAT.11	0.302	7.25

Table 5.3 shows the amount of copper contents on various catalysts which was measured by AA method. The data from the Table indicates that the copper contents of copper catalysts which was calcined at various temperatures were almost the same. It was indicated that there was no effect of vapour loss of copper metal from catalyst surface during the calcination. So, the reduced metal surface area was only resulted from the sintering of catalysts.

A reference catalyst in this experiment is a copper catalyst which was prepared by the same method as reported by Huang et al. [5]. From the data of catalysts characterization, CO adsorption capacity and specific electrical conductivity, it was seen that the SMSI effect of this catalyst (CAT.1) was lower than CAT.6 whereas its activity was higher than CAT.6 (see figure 5.1). This argument seems to indicate that another effect is also acting. From figure 5.2, it could be seen that CO_2 adsorbable strength of CAT.1 was lower than CAT.6. Retrospect to the mechanism of contact catalysis [48], when CO_2 (product from CO oxidation reaction) can be strongly adsorbed on the copper active sites, it will prevent CO and O_2 (the reactants of CO oxidation reaction) from reaching that copper active sites. In this case, hence, lower activity of CAT.6 might be caused by its higher CO_2 adsorbable strength.

Pertaining to the effect of the calcination temperature on CO oxidation activity of the catalysts, the following conclusions can be drawn from the result as discussed above: Increasing the calcination temperature in reducing atmosphere can produce an effect on copper catalysts by enhancing its activity but the catalyst will tend to lose their capacity for CO chemisorption. This was presumably resulted from the electronic effect which was induced by high temperature reduction (HTR) of copper-supported catalysts [49]. The data of specific electrical conductivity, as shown in Table 5.1, have confirmed that the support could be reduced by hydrogen at high temperature. Additionally, it was also found in this experiment that CO_2 adsorbable strength played an important role on catalytic property of copper catalyst for CO oxidation reaction.

5.2 Effect of Platinum on Copper Catalyst

In this part of experiment, it was intended to study the effect of platinum incorporation on copper catalyst. Method for the preparation of platinum containing copper catalyst was described in section 4.1.3.2. An expediently route for this study was to fix one parameter in the preparation method, in this case the calcination temperature of 500°C, the suitable calcination temperature for both platinum [55] and copper. Then the other two parameters would be varied to find the suitable value, as discussed below.

5.2.1 % Pt loading: In this section, period of calcination would be fixed and the variation of % Pt loading was done in the range of 0.05% to 0.5%. Activity of the prepared catalysts were tested by CO oxidation reaction and the best Pt loading was chosen for the remaining experiment.

5.2.2 Period of Calcination: The chosen catalyst from section 5.2.1 would be studied for the effect of calcination period in the range of 1 to 9 hours in this experiment.

The CO oxidation activity of these catalysts was used as a criterion to choose the best catalyst in the research. The characterization of a series of these catalysts was made as in section 5.1 and the results were discussed below.

5.2.1 Effect of % Pt Loading

Before all else, it was necessary to find out a suitable order of impregnation of the two metals, copper and platinum, on support. Three Pt-Cu/Al_2O_3 catalysts were prepared by co-impregnation, separative impregnation with Cu prior to Pt, and separative impregnation with Pt prior to Cu. The catalytic activity of the three catalysts were evaluated at the temperature that the conversion of CO reached 98 % (T_{98}). Conditions for calcination and results of T_{98} were shown in Table 5.4.

Table 5.4 Condition for preparing and varying the order of impregnation Pt-Cu/Al_2O_3 and the data of their catalytic activity

Order of impregnation	Time of 1st calcination in air (h)	Time of further calcination in reducing atmosphere (h)	T_{98}^{*} (°C)
coimpregnation	2	2^{**}	150
Pt prior to Cu	2	2^{***}	140
Cu prior to Pt	2	2^{***}	160

* T_{98} is defined as the temperature that the conversion of CO reached 98 %. It was measured by using 100 cc/min of gas mixture, consisting of 10 % by volume of CO and 90 % by volume of air, passed over 100 mg of catalyst and the hourly space velocity of the gas was about 20,000 h^{-1} in the same apparatus as mentioned in section 4.2.3.

** Further calcination was made immediately after the first calcination.

*** Further calcination was made after re-impregnation with the solution of chloroplatinic acid or copper nitrate was accomplished.

From the data of T_{98} as shown in Table 5.4, it was seen that the best method of impregnation was the separative impregnation with Pt prior to Cu because this catalyst gave the lowest temperature for reaching 98 % of CO conversion. The tendency of catalytic activity data (T_{98}) indicated that chlorine in chloroplatinic acid, precursor of platinum metal, has an effect on the catalytic activity. Because chlorine may poison a metal by forming a surface metal chloride, or it may enhance sintering via the formation of volatile metal chlorides [26]. From the results shown in Table 5.4, it could be concluded that effect of chlorine in chloroplatinic acid on copper would depend on the order of impregnation which resulted in the contact time between chlorine and copper and the time of calcination.

Figure 5.3 shows the comparison of CO conversion of three catalysts : CAT.1, CAT.6, and CAT.11. It was seen that the highest activity catalyst was CAT.11, platinum incorporated copper catalyst. CAT.1 and CAT.6, the reference catalysts, had lower activity, respectively. From the activity results, it indicated that platinum in the catalyst has a promoting effect on copper catalyst because platinum is the most effective metal for hydrogen spillover that can lower the reduction temperature of oxides significantly [46]. Consequently, the first assumption for the promoting effect of platinum on copper catalyst was the higher concentration of active sites on surface of CAT.11 that had been caused by the lower reduction temperature. Retrospect to the result and discussion of section 5.1, SMSI caused a large increase in CO oxidation activity of the catalyst for CO oxidation reaction, so the SMSI effect might also be induced in CAT.11, the second assumption. The reasons for the promoting effect of platinum on copper catalyst

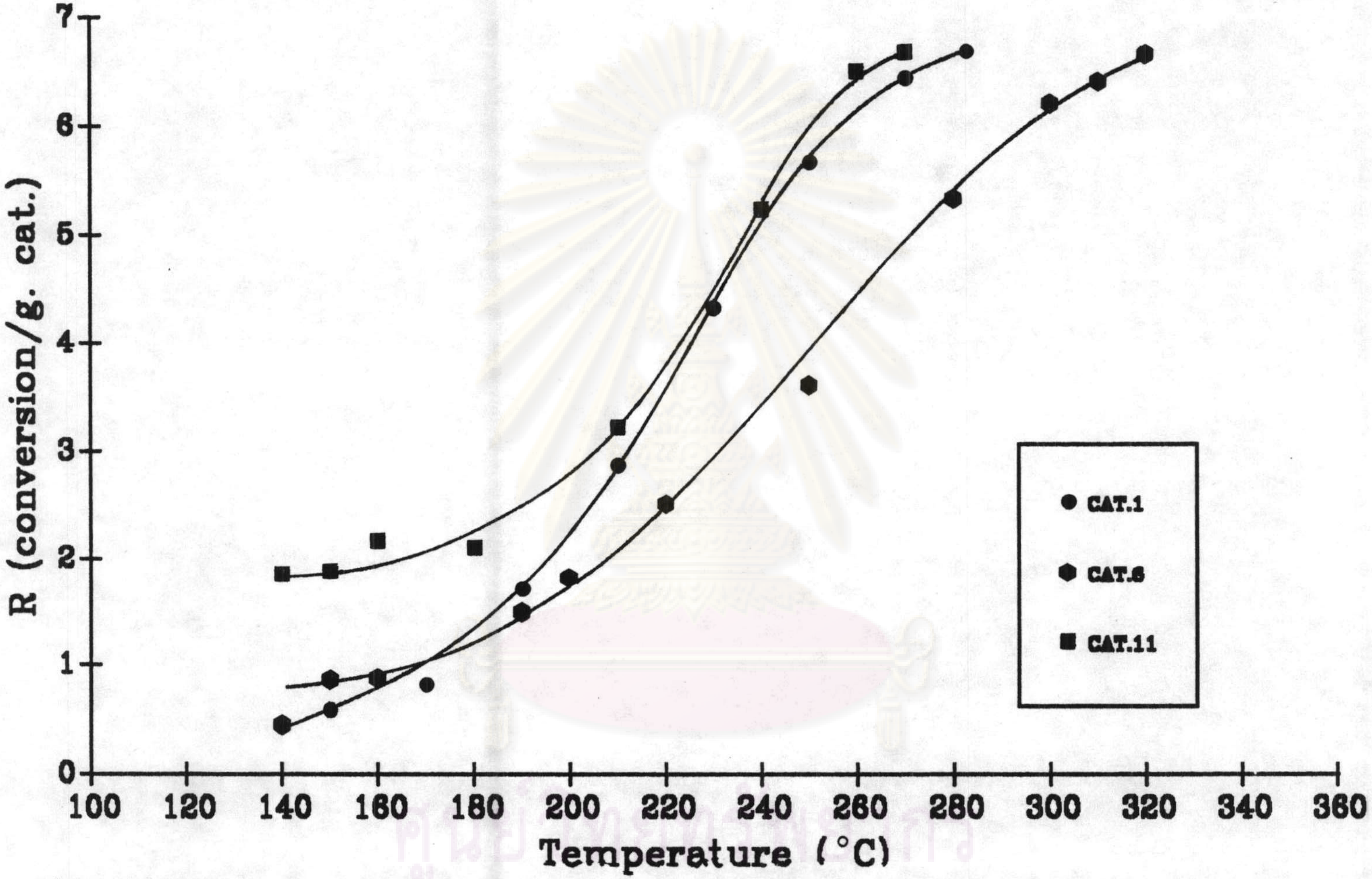

Figure 5.3 Activity in CO oxidation of copper catalysts compared to platinum incorporated copper catalyst: CAT.1 and CAT.6 were the copper catalyst prepared by Huang method [5] and the copper catalyst calcined in reducing atmosphere at 800 °C for 3 h., respectively. CAT.11 was the platinum incorporated copper catalyst calcined in reducing atmosphere for 7 h.

would be found out by the characterization of a series of platinum incorporated copper catalyst.

Figure 5.4 shows the CO conversion of platinum incorporated copper catalysts as a function of reaction temperature. It was seen from the figure that the activity of the catalyst was enhanced with the percentage of platinum loading in copper catalyst up to 0.3 wt%. This catalytic behavior could be explained that the increase of platinum loading (from 0 to 0.3 wt%) leads to the increased platinum dispersion so that the promoting effect of platinum on copper catalyst can occur throughout the surface of copper.

Gentry et al. [56] studied using TPR the reducibility of CuO with increasing contents of palladium. They showed that an increase in palladium amount allowed an easier reduction of CuO. The promoting effect of palladium on copper oxide reduction was explained by the easy reduction of Pd^{2+} to Pd° and the activation of hydrogen on metallic palladium. The activated hydrogen is then transferred to CuO, which is easily reduced.

In case of CAT.11, it was believed that the presence of platinum allowed an easier reduction of copper oxide. However, with platinum content more than 0.3 wt%, the activity of the catalyst was fallen down. This effect could be explained by the promoting effect of platinum on copper catalyst which does not exist throughout the surface of copper because the metal crystallite size for higher platinum loading would be bigger [57]. Therefore, the higher platinum content would result in the lower platinum dispersion on the surface [58]. Consequently, a suitable amount of

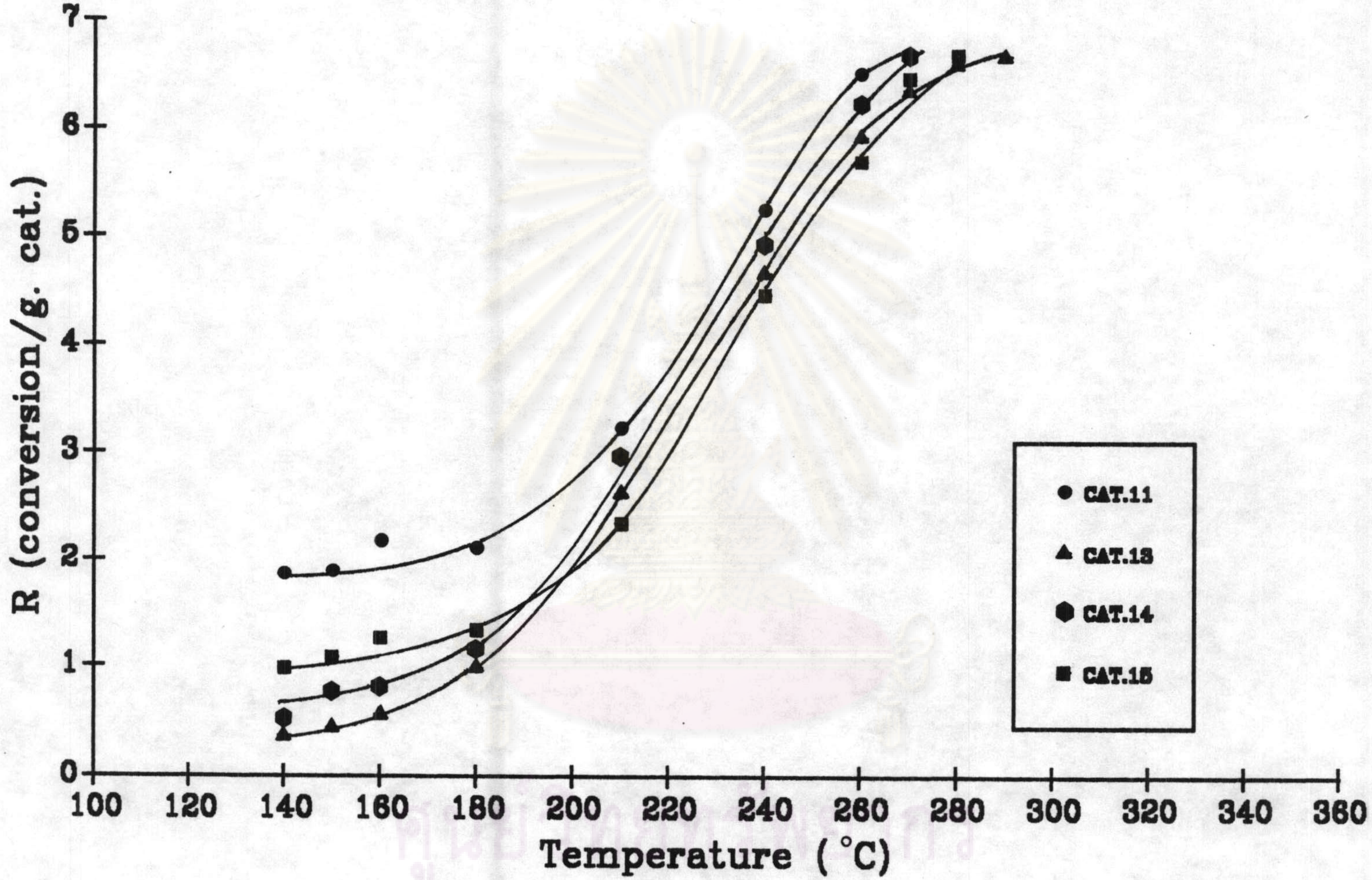

Figure 5.4 Activity in CO oxidation of platinum incorporated copper catalysts with various percentages of platinum loading: CAT.11, CAT.13, CAT.14, and CAT.15 were platinum incorporated copper catalyst having 0.3 wt%, 0.05 wt%, 0.1 wt%, and 0.5 wt% of platinum by catalyst weight, respectively.

platinum in platinum incorporated copper catalyst is 0.3 wt%. Period of calcination was the next parameter that would be studied.

5.2.2 Effect of Calcination Period on Platinum Incorporated Copper Catalyst

Like the other sections, activity test of the catalysts was the first method for selection of the best catalyst. In this section, effect of calcination period on platinum incorporated copper catalyst was studied and the result of activity test was shown in figure 5.5. From this figure, it was seen that the activity of the catalyst was increased as the calcination period was increased up to 7 hours. This result corresponded with the amount of metal active sites as shown in figure 5.7. It was seen from figure 5.7 that the amount of metal active sites were also increased as the calcination period was increased up to 7 hours. More than 7 hours of calcination periods, the augmentation of metal active site was very slightly.

Figure 5.6 shows the results of activity test of four catalysts; CAT.7, CAT.11, CAT.16, and CAT.17. From figure 5.6 (a), the lowest activity catalyst was CAT.16 which was prepared in oxide form. Thus, it could be concluded that calcination in reducing atmosphere produces a high activity platinum incorporated copper catalyst. From figure 5.6 (b), when the conversion of CAT.11, CAT.7, and CAT.16 were compared at the reaction temperature of 180 °C, it was obviously shown that synergistic effect existed in CAT.11.

Table 5.5 shows the results of catalysts characterization. The fourth column of the table shows the BET

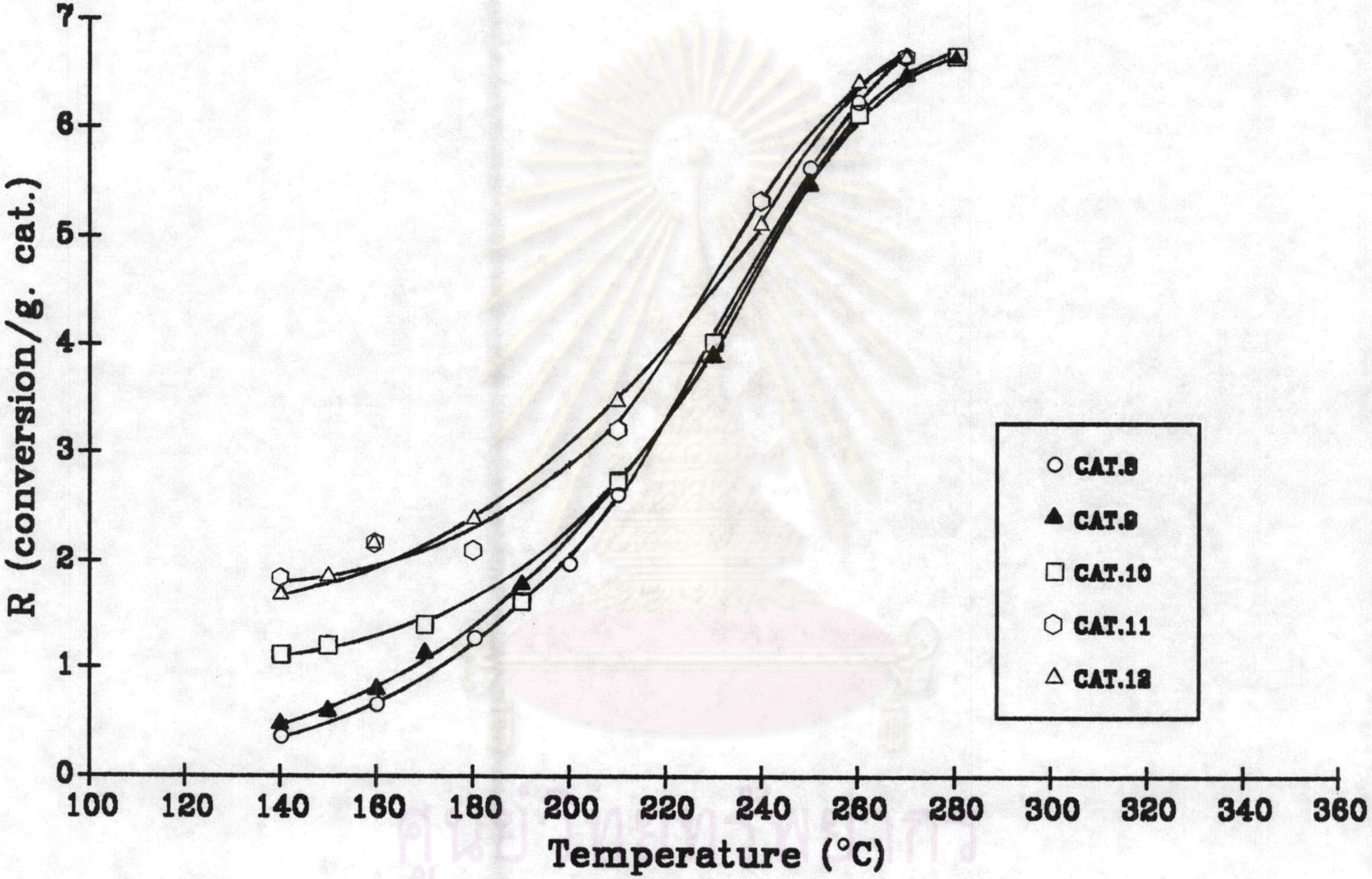

Figure 5.5 Activity in CO oxidation of platinum incorporated copper catalysts with various calcination periods: CAT.8, CAT.9, CAT.10, CAT.11, and CAT.12 were platinum incorporated copper catalysts calcined in reducing atmosphere for 1 h, 3 h, 5 h, 7 h, and 9 h, respectively.

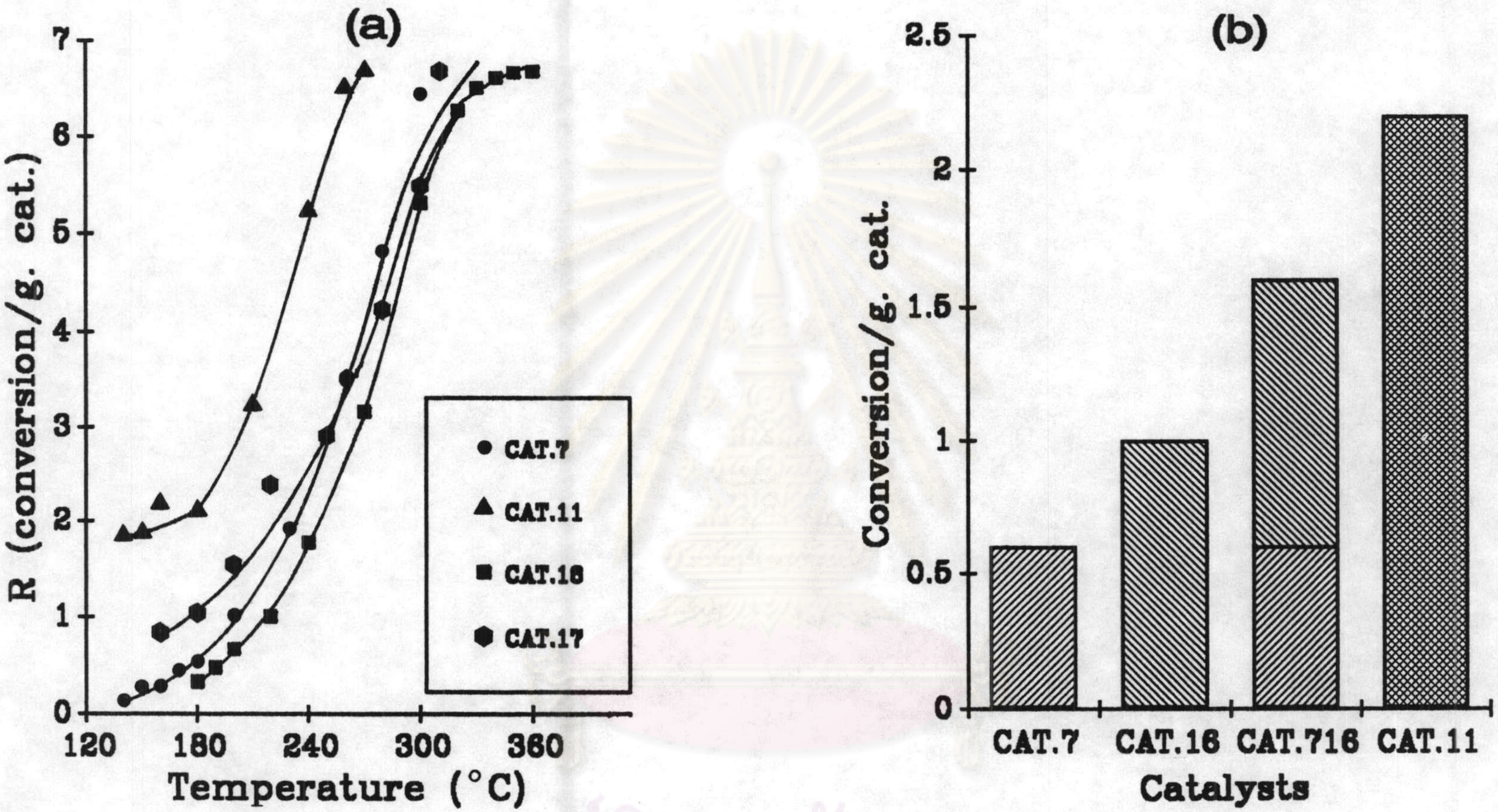

Figure 5.6 Synergistic effect in platinum incorporated copper catalyst

(a) Activity in CO oxidation of platinum incorporated copper catalysts

(b) Activity in CO oxidation of platinum incorporated copper catalysts at the reaction temperature of 180°C: CAT.7, CAT.11, and CAT.17 were Cu, Pt-Cu, and Pt catalysts, respectively. CAT.16 was Pt-Cu catalyst calcined in air. CAT.716 = Activity of CAT.7 + CAT.16.

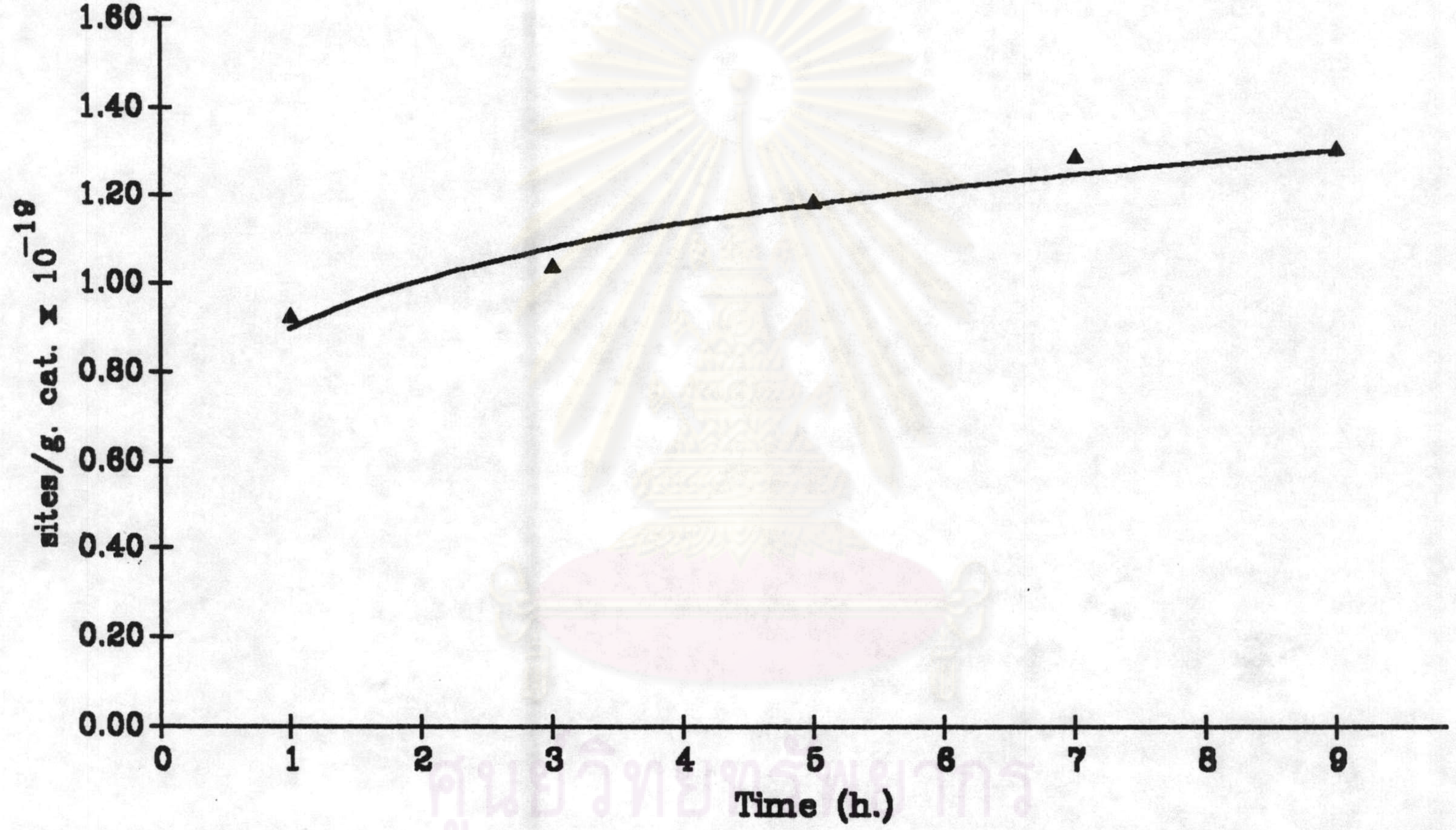

Figure 5.7 Metal active sites, measured by N_2O reaction, of platinum incorporated copper catalysts as a function of calcination periods in reducing atmosphere

Table 5.5 CO Adsorption Capacity, CO_2 Adsorption Capacity, CO_2 Adsorbable Strength, BET Surface Area and Specific Electrical Conductivity Data of Platinum Incorporated Copper Catalysts

Catalysts (ref. to Table 4.2)	CO Adsorption Capacity (μmol/g.cat.)	CO_2 Adsorption Capacity (μmol/g.cat.)	$t_{d,max}$ (°C)	BET (m^2/g.cat)	Specific Electrical Conductivity ($ohm^{-1}cm^{-1}$)
CAT.8	28.51	91.1	120	211.9	1.24×10^{-6}
CAT.9	27.85	75.1	110	209.5	1.29×10^{-6}
CAT.10	23.17	73.5	110	200.0	1.33×10^{-6}
CAT.11	19.13	71.6	90	199.4	1.47×10^{-6}
CAT.12	18.74	64.3	100	198.8	1.53×10^{-6}
CAT.16	134.43	139.9	140	209.3	0.79×10^{-6}

* $t_{d,max}$ is the CO_2 adsorbable strength which was expressed by the temperature at the maximum CO_2 desorption.

surface area of catalysts used to confirm that the type of CO or CO_2 adsorption is not a physical adsorption. Because N_2, used in BET method, is adsorbed on the sample by the physical adsorption [54]. It was obviously seen that, when compared CAT.16 to the others, BET data did not in consistent with the data of the amount of CO, CO_2 adsorbed on the catalyst. Therefore, the type of adsorption of CO, CO_2 was not a physical adsorption. For CAT.8-CAT.12, CO adsorption capacity decreased as the calcination period was increased while the values of specific electrical conductivity increased. The tendency of CO_2 adsorption capacity was similar to the tendency of CO adsorption capacity, the amount of adsorption capacity decreased as the calcination period was increased. From the results as shown in Table 5.5, it might be concluded that SMSI effect would probably occur in the platinum incorporated copper catalysts but it need further confirmation.

Figure 5.8 shows the comparison of TPD profile of CO_2 on five catalysts, CAT.8-CAT.12. It was seen that CO_2 adsorbable strength corresponded with the result of activity test as shown in figure 5.5. Because the results as shown in figure 5.8 were quite consistent with the results as shown in figure 5.5. This indicated that the CO_2 adsorbable strength also played an important role on the activity of platinum incorporated copper catalysts. The matter for consideration of the relation between catalytic activity and the value of CO_2 adsorbable strength were :

1. The higher CO_2 adsorbable strength, the lower catalytic activity.

2. If the value of CO_2 adsorbable strength of the catalysts were equal, the value of CO_2 adsorption capacity must be considered.

From all of the results discussed above, it was seen that SMSI effect would probably occur in the platinum incorporated copper catalysts. Retrospect to the characteristic data of copper catalyst (Table 5.1) and considering figure 5.3 again, an obvious argument was shown. If SMSI effect has occured in CAT.11, the catalyst should have CO adsorption capacity lower than CAT.1 and CAT.6 with higher value for specific electrical conductivity. But it

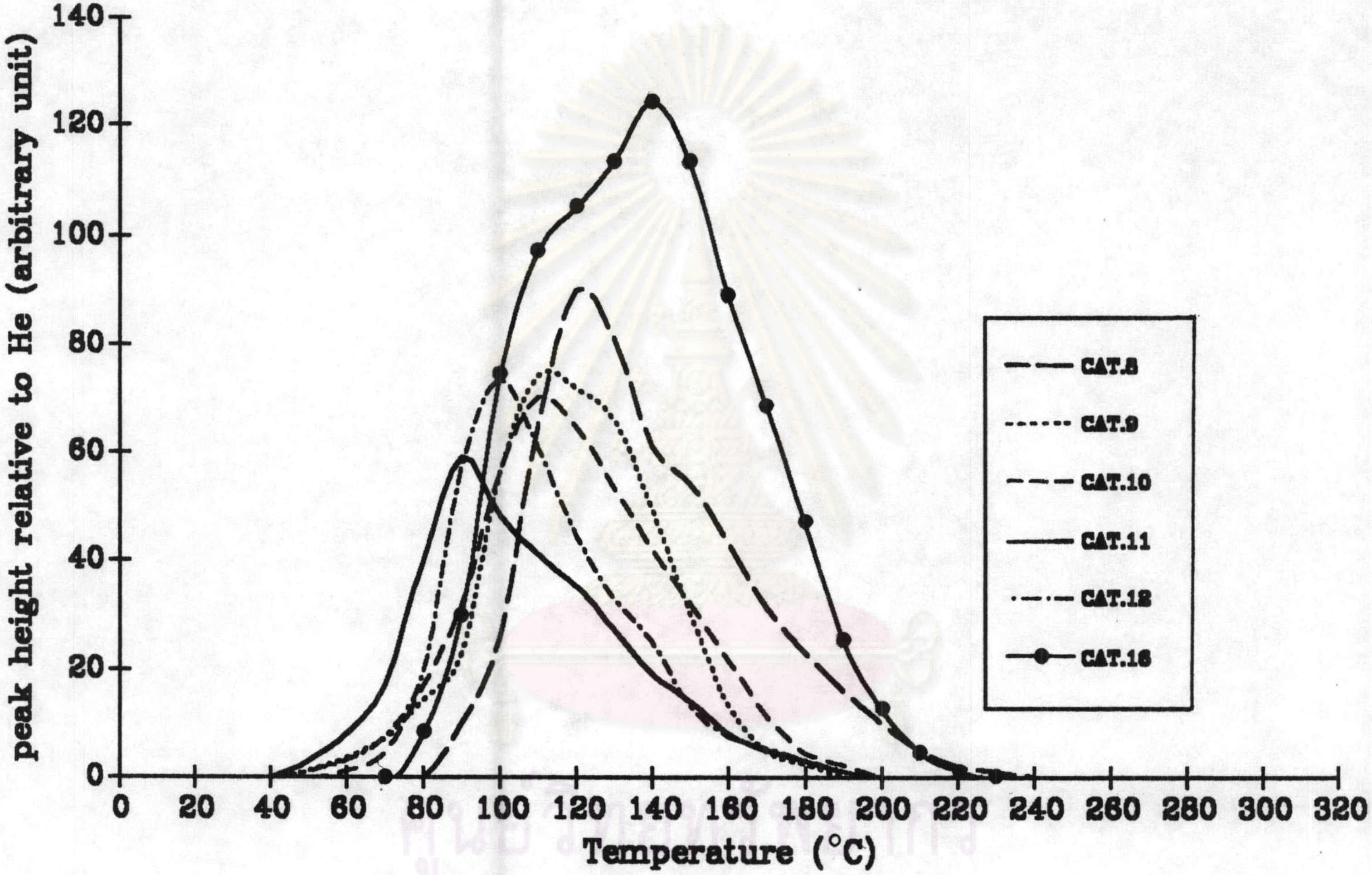

Figure 5.8 The temperature-programmed desorption profiles of CO_2 on platinum incorporated copper catalysts: CAT.8, CAT.9, CAT.10, CAT.11, and CAT.12 were platinum incorporated copper catalysts calcined in reducing atmosphere for 1 h, 3 h, 5 h, 7 h, and 9 h, respectively. CAT.16 was platinum incorporated copper catalyst calcined in air for 7 h.

found that the value of specific electrical conductivity were not in agreement with the activities of catalysts as shown in figure 5.3. Consequently, increasing in activity of CAT.11 should not have resulted from SMSI phenomena, the second assumption as mentioned in section 5.2.1 was rescinded. Further assumption apart from the first assumption in section 5.2.1 was the assumption of metal-metal interaction between platinum and copper. The result of further experiment for testing the remaining assumption would be discussed in the next section in detail.

5.3 Metal-Metal Interaction in Platinum Incorporated Copper Catalyst

In this research, metal-metal interaction between platinum and copper was observed by using the method as mentioned in section 4.3.5.3. Because carbon monoxide chemisorption on Cu is weak and reversible [50], therefore it can be assumed in the condition of this study that all of carbon monoxide molecules are only adsorbed on the surface of platinum.

Table 5.6 shows the result of CO chemisorption on platinum in platinum incorporated copper catalysts. The data from the table obviously indicates that platinum and copper were in close contact and probably had an interaction with each other. CO chemisorption behavior of platinum in platinum incorporated copper catalysts was altered after the copper metal in the catalysts reacted with N_2O. This characteristic result might be described by the two proposed explanations : alloy model and geometric dilution model.

A point of view of the first hypothesis, alloy model, is that both the platinum and copper metals were uniformly dispersed on

Table 5.6 CO Chemisorption on Platinum in Platinum Incorporated Copper Catalysts

Catalysts (ref.to Table 4.1 and 4.2)	CO adsorption before reaction with N_2O (molecule/g. cat)	no. of reacted N_2O (molecule/g. cat.)	CO adsorption after reaction with N_2O (molecule/g. cat.)
CAT.7	-	0.44×10^{19}	-
CAT.8	0.66×10^{19}	0.92×10^{19}	1.64×10^{19}
CAT.9	0.82×10^{19}	1.03×10^{19}	2.25×10^{19}
CAT.10	0.91×10^{19}	1.18×10^{19}	2.13×10^{19}
CAT.11	0.98×10^{19}	1.28×10^{19}	1.98×10^{19}
CAT.12	0.95×10^{19}	1.29×10^{19}	2.01×10^{19}
CAT.16	1.45×10^{19}	1.89×10^{19}	2.52×10^{19}
CAT.17	1.46×10^{19}	0.46×10^{19}	-

the support and they formed the bimetallic clusters (see figure 5.9 (a)). When CO was induced onto the surface of the catalysts, some of CO molecules were adsorbed by platinum on the surface but they could not be adsorbed by platinum in bimetallic bulk form. The decomposition of a nitrous oxide molecule on copper surface which is accompanied by the liberation of one nitrogen molecule according to the reaction [16];

$$N_2O\ (g) \quad + \quad 2\ Cu_s \quad \longrightarrow \quad N_2\ (g) \quad + \quad (Cu\text{-}O\text{-}Cu)_s$$

It was believed that the copper metals at the surface

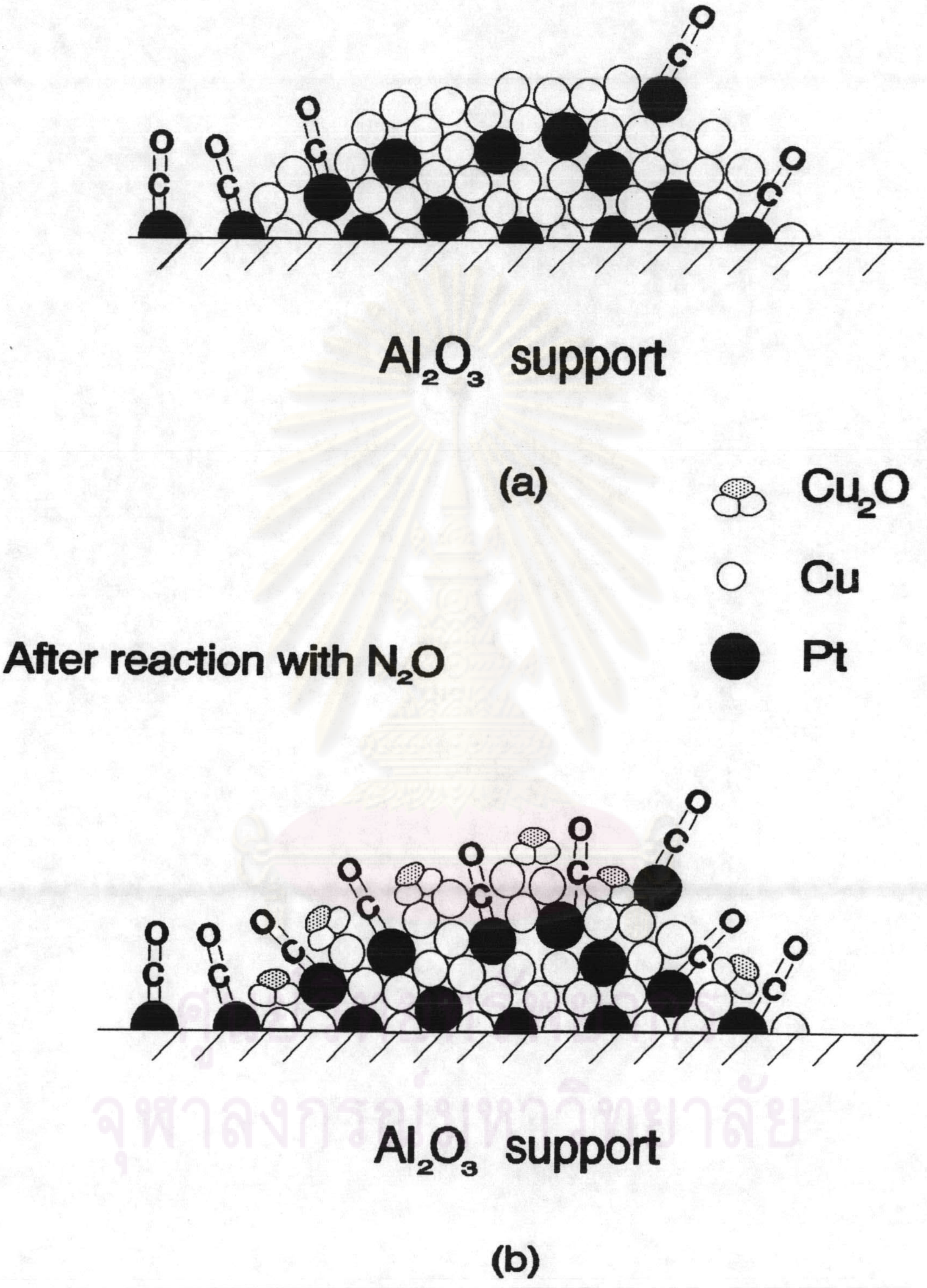

Figure 5.9 Alloy Model

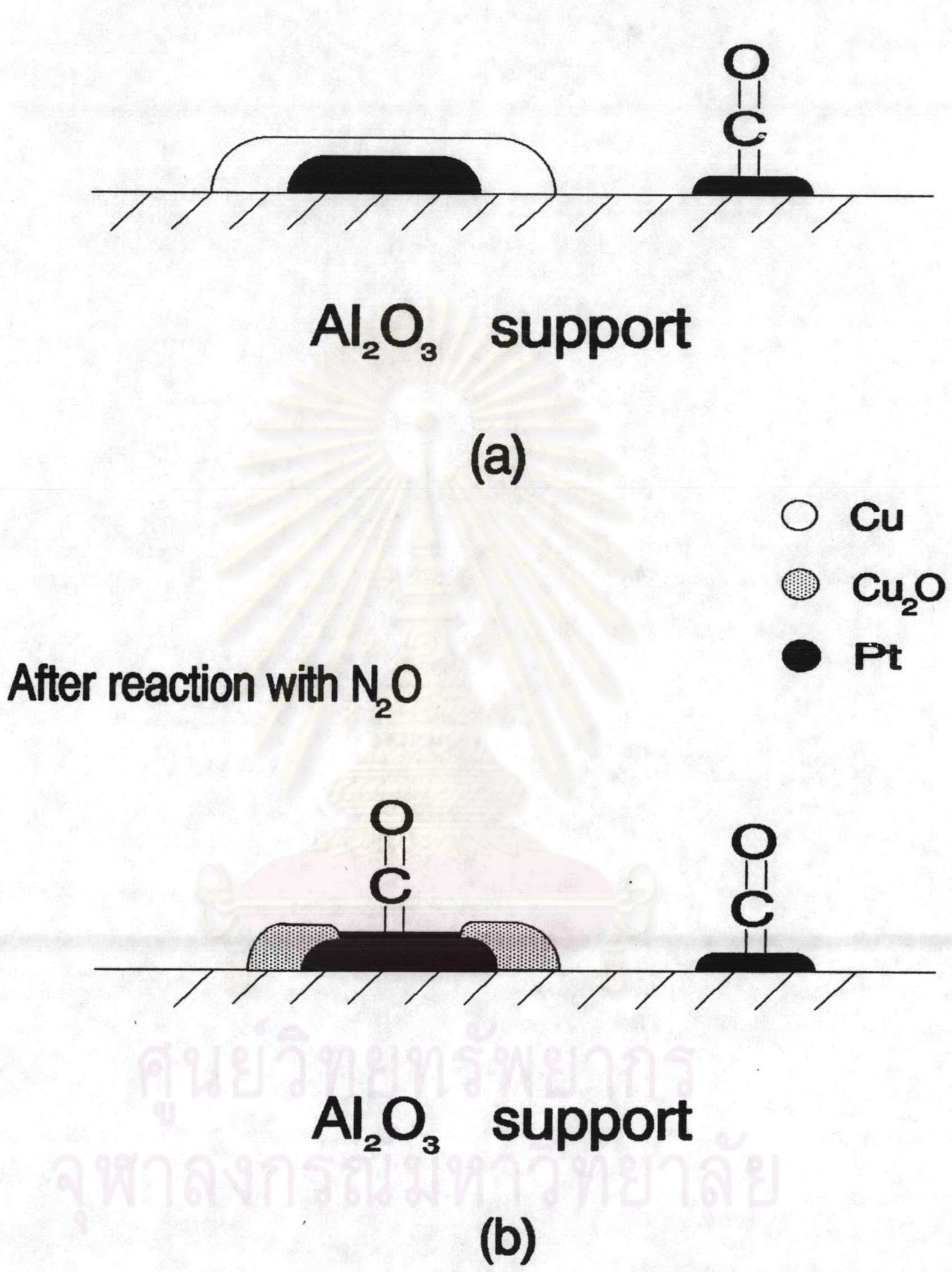

Figure 5.10 Geometric Dilution Model

undergoing the reaction with N_2O was segregated to form Cu_2O and create the hole through the surface to platinum in bimetallic bulk. Therefore, after reaction with N_2O, the amount of adsorbed CO is augmented because CO molecule can diffuse through the created hole to adsorb on platinum in the bulk (see figure 5.9 (b)).

In addition to alloy model, geometric dilution model can also explain the phenomena of CO chemisorption of platinum in platinum incorporated copper catalysts. For geometric dilution model, platinum and copper were formed in monometallic clusters. Some of copper cluster clung to platinum clusters and cause a blocking of a fraction of surface platinum by copper (see figure 5.10 (a)). Therefore, only unblocked platinum can adsorb CO molecules. Figure 5.10 (b) shows the segregation of copper surface due to the formation of Cu_2O after the decomposition of N_2O on copper surface. The formation of Cu_2O may create a hole through copper layer to platinum clusters and bring about the greater amount of adsorbed CO molecules.

For the two proposed models as above-mentioned, the alloy model was more possible than the geometric dilution model. The results from Table 5.6 shows that copper catalyst (CAT.7) and platinum incorporated copper catalyst (CAT.11) that using the same preparation condition had a large difference in the amount of Cu surface active sites (determined by reaction with N_2O). It was seen that new sites were created in CAT.11 and in agreement with Tomanek et al. [59] who have shown that the alloy surface of Pt-Cu alloys are only moderately enriched in Cu. If the geometric dilution model was possible, the amount of Cu surface active sites should not be altered.

Retrospect to the data of CO adsorption capacity of the platinum incorporated copper catalysts as shown in Table 5.5, it could be explained by the electronic effects. The feature of an electronic effects used to explain the phenomena is the same as used for bimetallic Pd-Cu catalyst [25]. For this explanation, electrons were donated from copper to platinum and brought about higher oxidation state copper. In this manner, the amount of Cu^{2+} was augmented causing the suppression of CO adsorption capacity because CO had been shown to adsorb on Cu^{+} strongly, but weakly on Cu^{2+} [60].

H.G.J. Lansink Rotgerink et al. [61] have explained that, for CO/H_2 reaction, SMSI catalysts have a large activity because the heat of adsorption of carbon monoxide is lowered compared to the normal situation and the hydrogen is adsorbed more strongly. In this way, hydrogen can compete better with carbon monoxide for an adsorption site and the coverage of hydrogen on the catalyst surface is increased. According to H.G.J. Lansink Rotgerink et al., in the case of this experiment, a high activity SMSI catalyst (CAT.1) can be explained by the same explanation. When the heat of adsorption of carbon monoxide is lowered compared to the normal situation, oxygen can compete better with carbon monoxide for an adsorption site and the coverage of oxygen on the catalyst surface is increased.

For platinum incorporated copper catalysts, two postulations can explain why its activities were increased. The first postulation was an enhancement of Cu surface active sites which was caused by an alloy formation between platinum and copper. The second postulation was an interaction between platinum and copper which caused the phenomena similar to SMSI phenomena, the suppression of CO adsorption capacity.