CHAPTER 5

RESULTS AND DISCUSSION

In this chapter, the experimental results and discussion are divided into three sections: section 5.1) characterization of low temperature coke deposit on metal sites of platinum catalyst, section 5.2) effect of promoter on activity of the catalyst, section 5.3) effect of promoter on low temperature coke deposit on metal sites.

5.1 Characterization of low temperature coke deposit on metal sites of platinum catalyst.

5.1.1 Low temperature coke on metal active site.

Figure 5.1 shows temperature programmed oxidation profiles of Pt/Al_2O_3 catalyst. There are two sharp peaks around 190-250 $^\circ$C, 430-450 $^\circ$C and a shoulder around 350-380 $^\circ$C . In previous work, Barbier (1987) described a shoulder and the last peaks as coke on metal and coke on support respectively. The first peak of TPO profile which easily oxidized at low temperature maybe reversible coke on metal site that can be removed by hydrogen(Sormorjai and Salmeron, 1982). To prevent the confusing about this type of coke, it should be named as low temperature coke on metal active site. On the other hand, the remain coke on metal active site after regeneration is defined as high temperature coke .
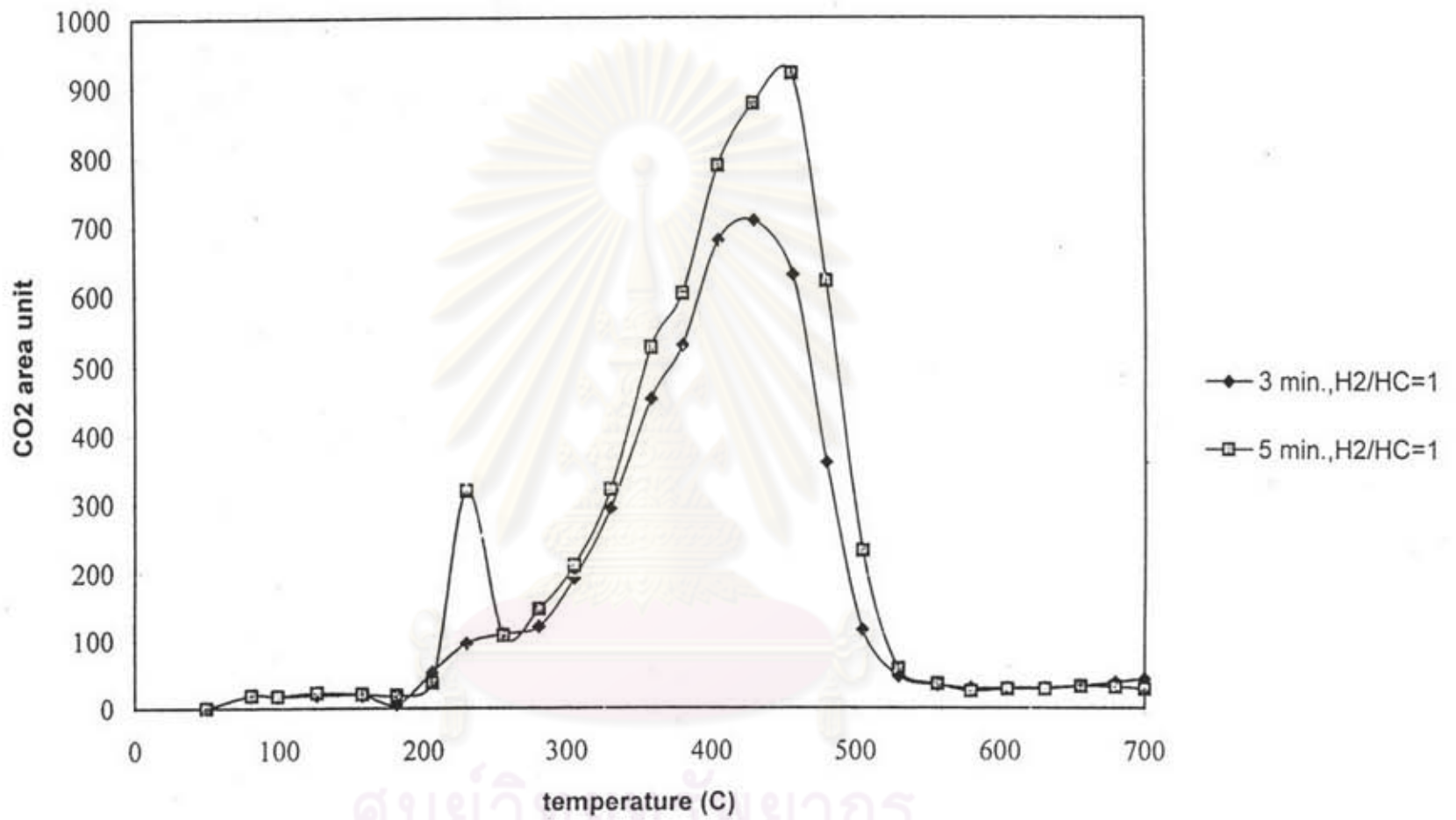
Figure 5.1 Temperature programmed oxidation of Pt/Al_2O_3 at 3 and 5 minutes on stream, reaction temperature 500 $^{\circ}$C, H_2/HC=1, 20%propane in N_2 balance, GHSV=22,525 hr^{-1}

To confirm this hypothesis, Pt/Al_2O_3 coked catalyst was regenerated at various temperature and the regenerated catalyst was measured metal active sites by CO adsorption technique. The result are shown in figure 5.2 . Three zones of coke combustion were observed. The first zone between 150-250 ^{o}C, metal active sites are slightly recovered thus it has low value of slope. This zone was referred to low temperature coke on metal active sites. Then increasing regeneration temperature lead to sharply increase of active sites until 350 ^{o}C. Higher regeneration temperature than 350 ^{o}C, the active sites rather constant. These results agree with coke formation model which proposed by Siripoln(1995). Coke formation during dehydrogenation reaction occurs in four steps.

Step 1 : Propane is adsorbed on the metal active site, series of fragmentation and dehydrogenation reaction lead to low temperature coke formation on the low temperature coke site

Step 2 : On the low temperature coke site, low temperature coke migrates to high temperature coke site then transforms to high temperature coke by hydrogen removal.

Step 3 : Coke precursor, low temperature coke and high temperature coke drain-off from metal site to support.

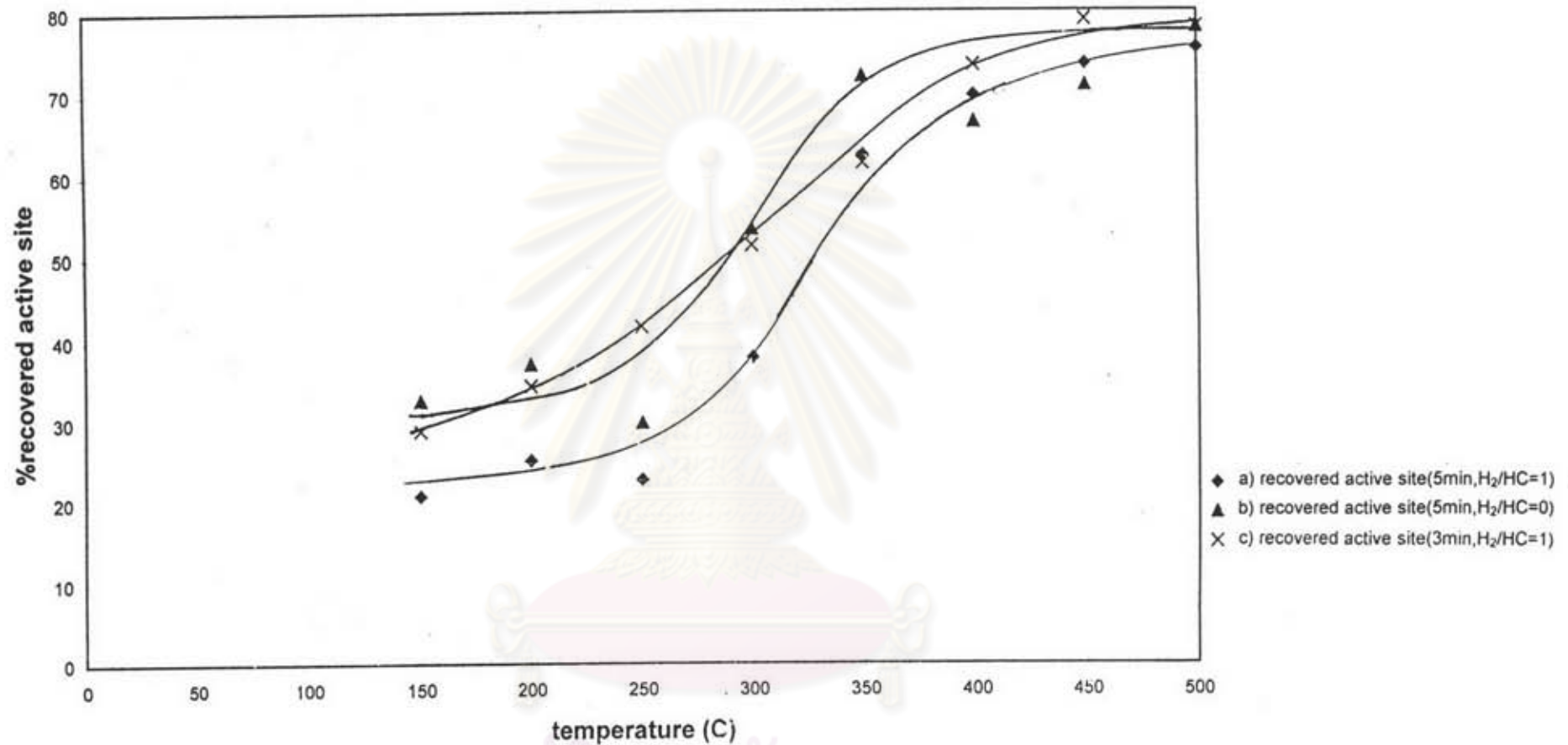Step 4 : Low temperature coke on support transforms to high temperature coke by hydrogen removal.

Figure 5.2 %Recovered active site of Pt/Al$_2$O$_3$ catalyst at reaction temperature 500 ^{o}C, 20%propane in N$_2$ balance, GHSV=22,525 hr^{-1} after regenerated at various temperature,
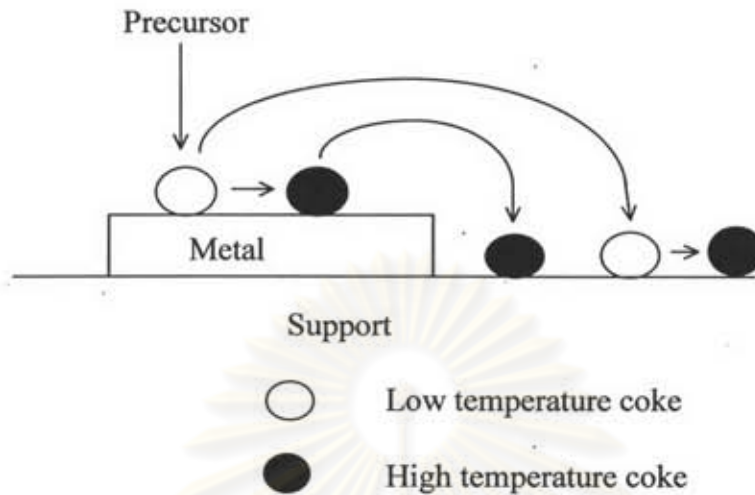
Figure 5.3 The proposed model for coke formation (Siripoln,1995)

5.1.2 The effect of hydrogen and time on stream

Curve (a) and curve (b) in figure 5.2 have the same conditions except H_2/HC ratio. Comparison between curve (a) and curve (b) give the effect of hydrogen on the nature of coke on metal active site. It was found that the addition of hydrogen to feed stream reduce low temperature coke on metal active site thus reduce coke which will be convert to high temperature coke. This result agree with Biswas et.al. (1987) who suggested the effect of hydrogen to coke deposit on metal active site. The presence of hydrogen in feed stream can clean up coke on metal active site by catalytic hydrogenation and catalytic hydrogasification.

Effect of time on stream of dehydrogenation is also investigated. It is found that curve (c) which demonstrates coke on metal active site at reaction time 3 minutes does not clearly distinguish the type of coke. This phenomenon possibly due

to the incomplete development of low temperature coke to more graphitic coke. In the early stage of coke deposition on metal active site, the majority of coke deposit is low temperature coke(Biswas et.al.,1987). Hence, at low regeneration temperature coke of 3 minutes on stream is more regenerated than coke of 5 minutes on stream. However, the recovered active sites at high regeneration temperature of both time on stream are not different.

5.2 Effect of promoter on activity of the catalysts

Dehydrogenation catalyst always be deactivated by coking during reaction period. Pt/Al_2O_3 catalyst which is used for propane dehydrogenation in this study has high activity but also be deactivated very fast by coking. Addition of a second metal such as tin improve the activity and selectivity of the catalyst. Furthermore, addition of alkali metal can further improve the activity of the Pt-Sn catalyst. Figure 5.4 shows the conversion of propane on 0.3(wt)%Pt/Al_2O_3, 0.3(wt)%Pt-0.3(wt)%Sn/Al_2O_3 and 0.3(wt)%Pt-0.3(wt)%Sn-0.6(wt)%K/Al_2O_3. It is found that the conversion of Pt/Al_2O_3 catalyst rapidly decreases while Pt-Sn-K/Al_2O_3 and Pt-Sn/Al_2O_3 catalyst can maintain their activity. The reason of this phenomena is the reduction of coke when adding tin and potassium to Pt/Al_2O_3 catalyst. Figure 5.5 shows percentage of metal active sites covered by coke. The results show that active sites of Pt/Al_2O_3 is covered more than Pt-Sn and Pt-Sn-K catalyst. Many study have been made to explain the effect of tin and potassium as promoters. Addition of tin affects Pt/Al_2O_3 as : (1) decreases size of platinum ensemble (2): poisons acidic site of alumina support (3): reduces the strength of chemisorption of the hydrocarbons on metal surface(L. Liwu et.al.,1991). Hence, Pt-Sn catalyst can reduce coke deposit on metal active site by improving the migration of coke from metal to support. Because of the decreasing size of platinum ensemble hydrogenolysis, isomerization or coking reaction are also suppressed. Therefore, addition of tin increase the selectivity of the catalyst as shown in figure 5.6 which present the selectivity of Pt, Pt-Sn and Pt-Sn-K catalysts.
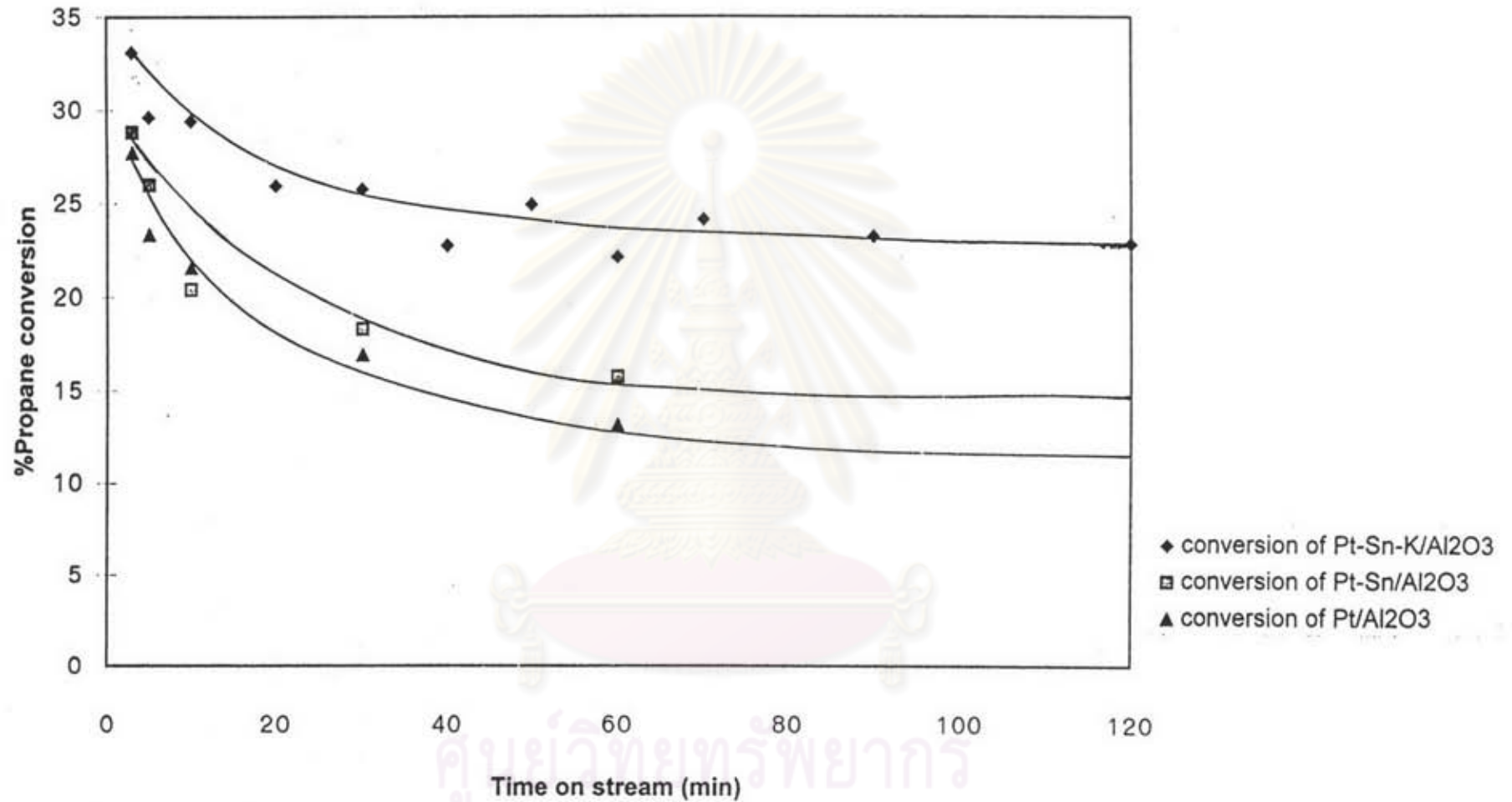
Figure 5.4 %Propane conversion on Pt/Al$_2$O$_3$, Pt-Sn/Al$_2$O$_3$ and Pt-Sn-K/Al$_2$O$_3$ at reaction temperature 500 $^\circ$C, H$_2$/HC=1, 20%propane in N$_2$ balance, GHSV=22,525 hr^{-1}
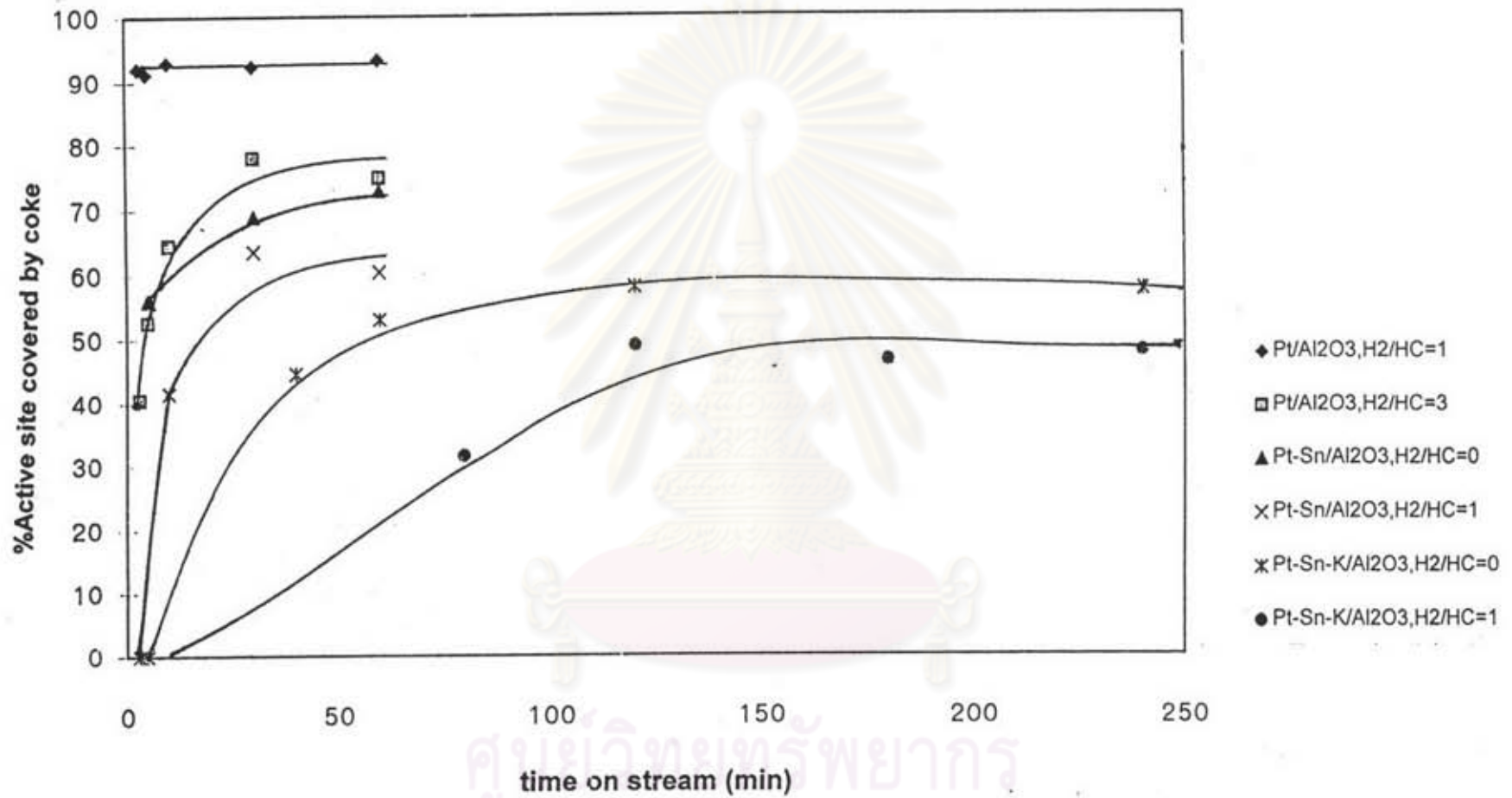
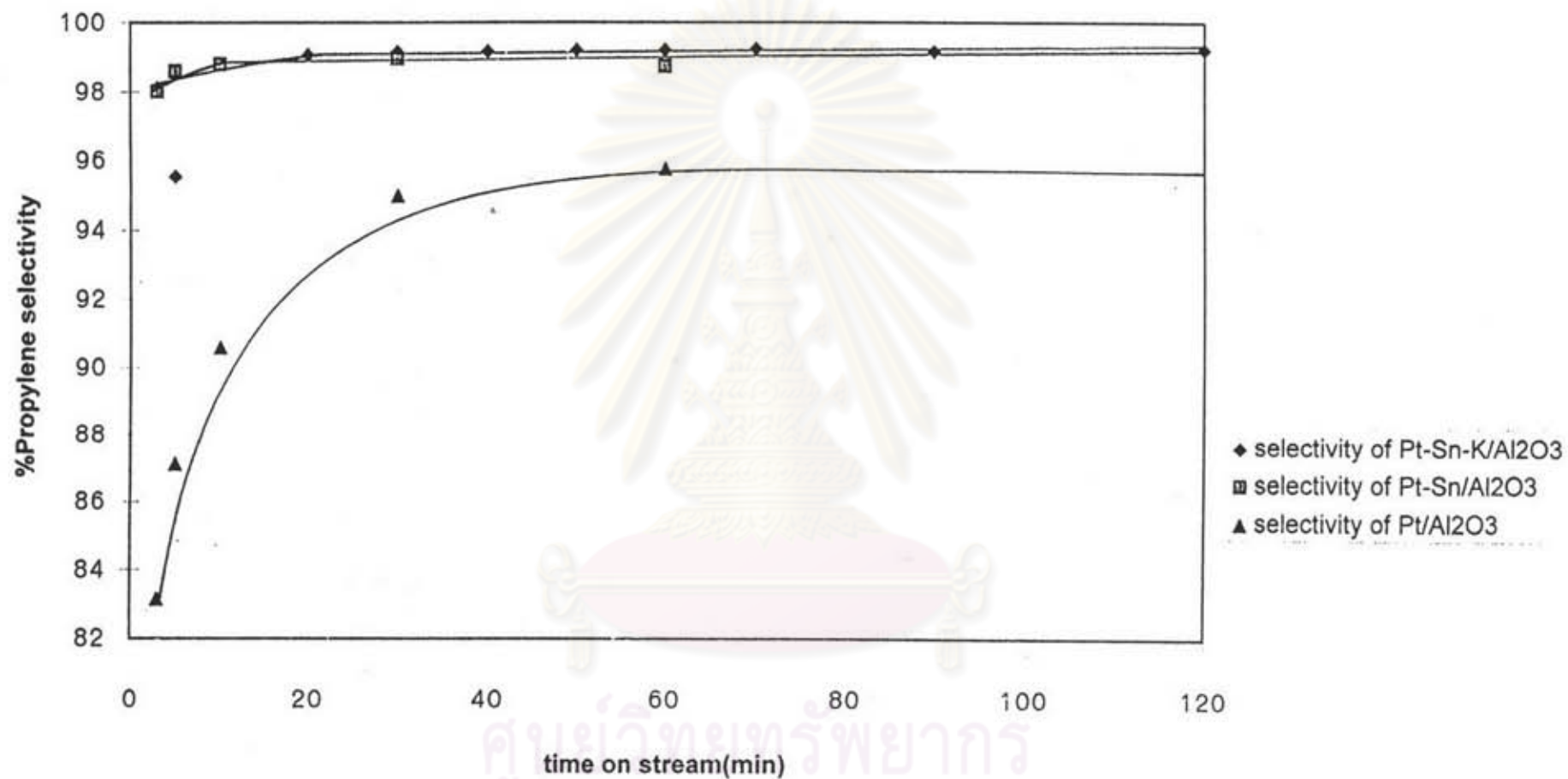Figure 5.5 %Active site covered by coke at reaction temperature 500 °C, 20%propane in N_2 balance, GHSV=22,525 hr^{-1}

Figure 5.6 %Propylene selectivity on Pt/Al$_2$O$_3$, Pt-Sn/Al$_2$O$_3$ and Pt-Sn-K/Al$_2$O$_3$ at reaction temperature 500 °C, H$_2$/HC=1, 20%propane in N$_2$ balance, GHSV=22,525 hr^{-1}

R.D. Cortright et.al.(1995) who investigated the effect of potassium to isobutane dehydrogenation catalyst found that addition of potassium to Pt-Sn/SiO$_2$ catalyst led to the formation of smaller platinum ensemble and further reduced acidic sites. They also found the enhancement of hydrogen adsorption when added potassium to Pt/SiO$_2$ and Pt-Sn/SiO$_2$ catalyst. Figure 5.5 clearly shows that addition of potassium to Pt-Sn/Al$_2$O$_3$ can further reduce coke coverage on metal active sites than Pt-Sn without potassium catalyst or potassium can promote metal cleaning function besides modify acidic function of the support. Thus, it can be postulated that the cleaning function of potassium is due to hydrogen spillover phenomena.

Plotting between %propane conversion and active sites of used Pt/Al$_2$O$_3$, Pt-Sn/Al$_2$O$_3$ and Pt-Sn-K/Al$_2$O$_3$ catalysts are shown in figures 5.7-5.9 respectively. The initial activity are obtained by extrapolating from the origin to the condition where the number of active sites equal to the fresh one. It is found that Pt/Al$_2$O$_3$ has the highest initial conversion but Pt-Sn/Al$_2$O$_3$ and Pt-Sn-K/Al$_2$O$_3$ have the similar value. Fresh active sites of these catalysts are shown in table 5.1. It can be seen that Pt catalyst has the highest active sites. Addition of Sn to Pt/Al$_2$O$_3$ decreases active sites and it further decrease when K is added to Pt-Sn/Al$_2$O$_3$. On the contrary, calculating initial turnover number of the three catalyst indicate that initial turnover number of Pt-Sn-K/Al$_2$O$_3$ is the highest. Turnover number of Pt-Sn/Al$_2$O$_3$ is lower whereas Pt/Al$_2$O$_3$ is the lowest. Therefore, the promoters have the influence to the active site of the catalyst although Pt/Al$_2$O$_3$ has the highest fresh active sites. These results are confirmed by the previous study by B.Jaikaew(1995) who studied the electrical conductivity of Pt/Al$_2$O$_3$, Pt-Sn/Al$_2$O$_3$ and Pt-Sn-K/Al$_2$O$_3$ catalyst.
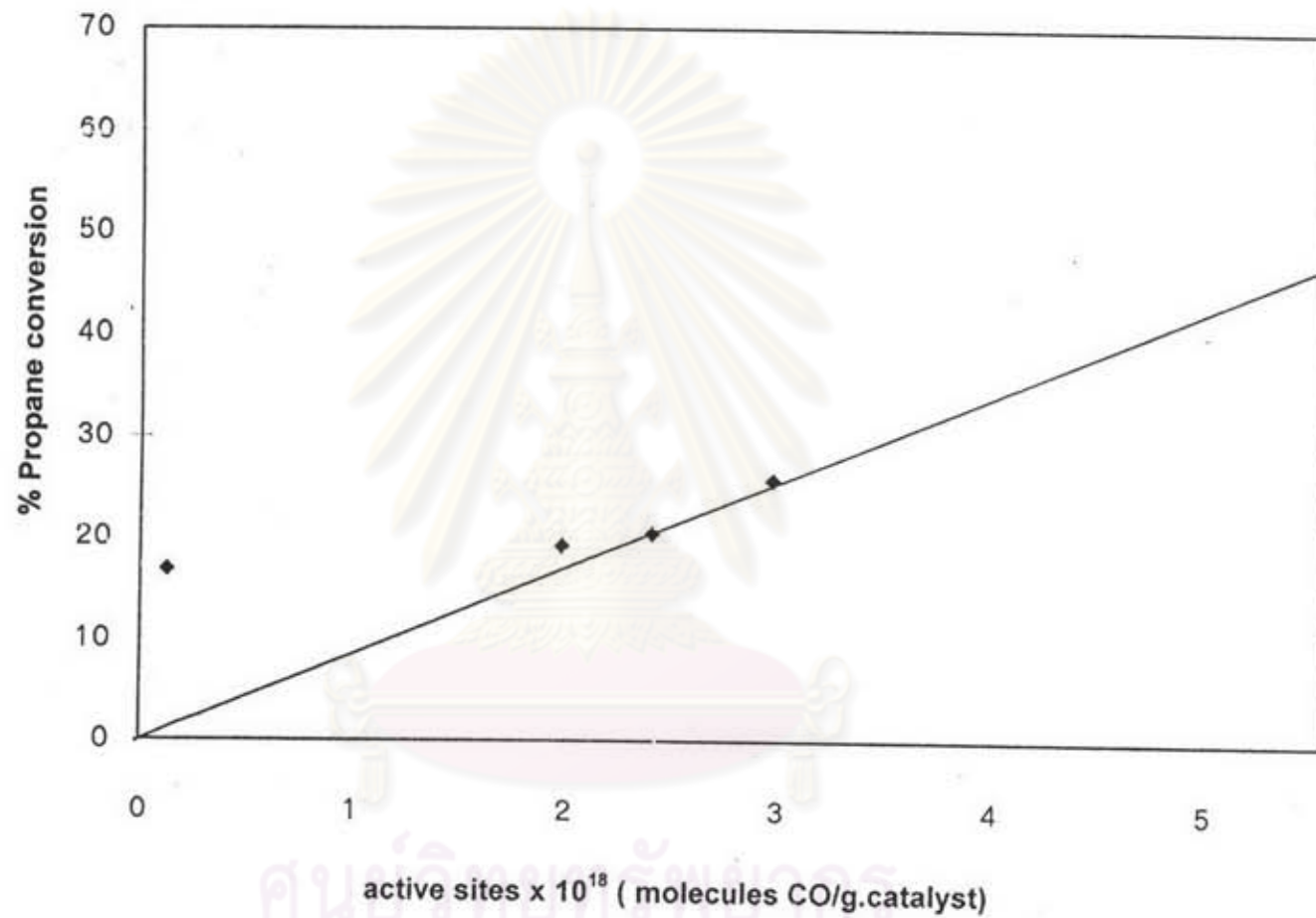
Figure 5.7 %Propane conversion and active sites of Pt/Al$_2$O$_3$ at reaction temperature 500 °C, GHSV=22,525 hr^{-1} , 20%propane in N$_2$ balance
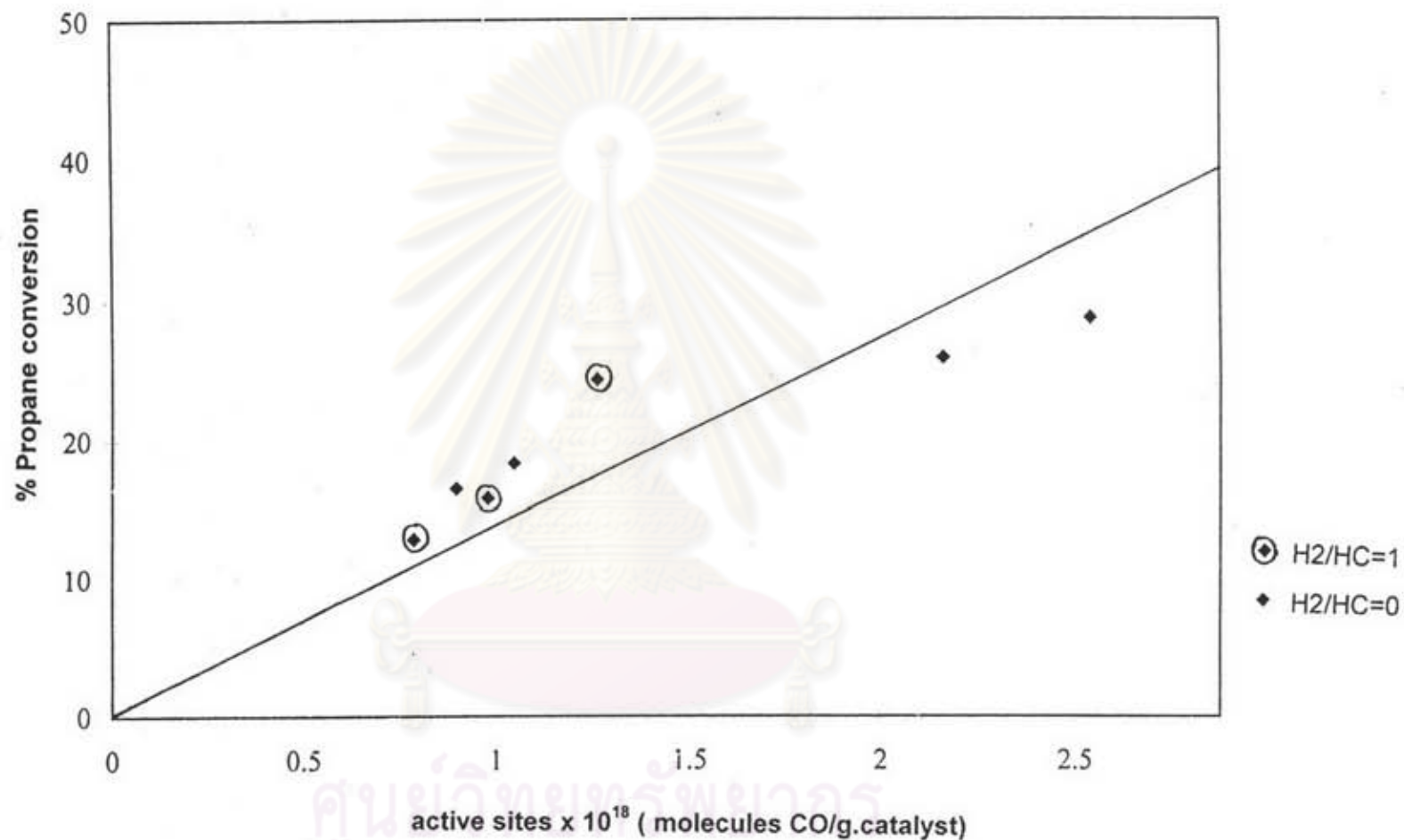
Figure 5.8 %Propane conversion and active sites of Pt-Sn/Al$_2$O$_3$ at reaction temperature 500 $^{\circ}$C, GHSV=22,525 hr^{-1} ,20%propane in N$_2$ balance
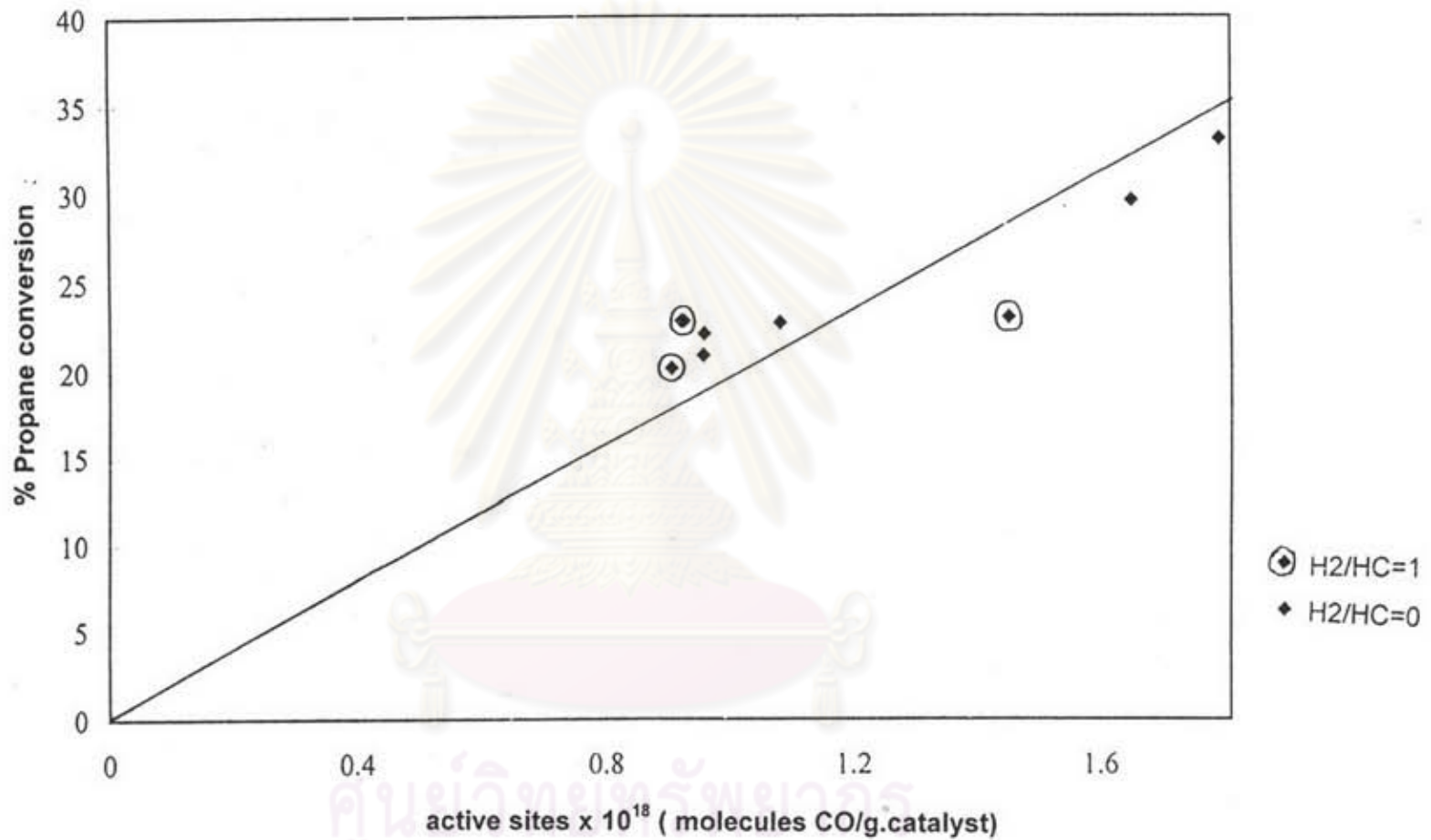
Figure 5.9 %Propane conversion and active sites of Pt-Sn-K/Al$_2$O$_3$ at reaction temperature 500 °C, GHSV=22,525 hr^{-1} ,20%propane in N$_2$ balance

Table 5.1 Metal active site of fresh catalyst, initial conversion and turnover number

Catalyst	Metal active sites of fresh catalyst (Molecules CO/g.cat)	Initial propane conversion at time=0 (%)	Turnover Number of the catalyst
0.3%Pt/γ-Al$_2$O$_3$	5.55x10^{18}	47	0.085
0.3%Pt-0.3%Sn/γ-Al$_2$O$_3$	2.88x10^{18}	39	0.135
0.3%Pt-0.3%Sn-0.6%K/γ-Al$_2$O$_3$	1.81x10^{18}	35	0.194

B. Jaikeaw (1995) found that Pt-Sn/Al$_2$O$_3$ and Pt-Sn-K/Al$_2$O$_3$ catalysts have excess electron(in conductivity unit, Ohm^{-1}.cm^{-1}) occurrence in the bulk of both catalysts as shown in table 5.2. Hence, it can be postulated that synergistic effect of tin and potassium addition on performance of catalyst is due to the excess electron that make platinum active sites stronger for dehydrogenation reaction.

Table 5.2 Excess electron of the catalysts (Bualom, 1995)

Catalyst	Excess electron in conductivity unit ($Ohm^{-1}.cm^{-1}$)
Pt/Al_2O_3	0
$Pt\text{-}Sn/Al_2O_3$	5.3×10^{-6}
$Pt\text{-}Sn\text{-}K/Al_2O_3$	15.3×10^{-6}

5.3 Effect of promoter on low temperature coke deposit on metal active sites

Since the promoters have effect on active site and coke deposition, this study investigated the influence of promoter on low temperature coke deposit on metal active sites. Figures 5.9-5.11 show % active sites covered by low temperature coke of Pt/Al_2O_3, $Pt-Sn/Al_2O_3$ and $Pt-Sn-K/Al_2O_3$ respectively. It is found from figure 5.9 that in the early time on stream of Pt/Al_2O_3 a number of active sites is covered by low temperature coke. Longer time on stream the low temperature coke continuously decrease by the transformation to high temperature coke until reaching an asymptote value. Since mixing hydrogen to feed stream can reduce coke on metal site, low temperature coke is also lowered. The increase of time on stream with presence of hydrogen in feed stream leads to the increase of low temperature coke and total coke. However, at 10 minutes on stream the amount of low temperature coke reaches a maximum value then it continuously decreases to asymptote value while the total coke still increases to a maximum value at about 30 minutes on stream.

Figure 5.10 shows the percentage of low temperature coke deposits on $Pt-Sn/Al_2O_3$ catalyst. It is found that Pt-Sn catalyst has the similar behavior to Pt catalyst but for the condition of $H_2/HC = 1$ the maximum value of low temperature coke is at 30 minutes on stream. Hence, addition of Sn can reduce low temperature coke deposit on metal active sites by shifting it to the longer time on stream. On the other hand, the pattern of low temperature coke of $Pt-Sn-K/Al_2O_3$ with $H_2/HC=0$ is similar to $Pt-Sn/Al_2O_3$ catalyst as shown in figure 5.11. The maximum value of $Pt-Sn-K/Al_2O_3$ is around 70-100 minutes on stream. When hydrogen is added to the feed stream the
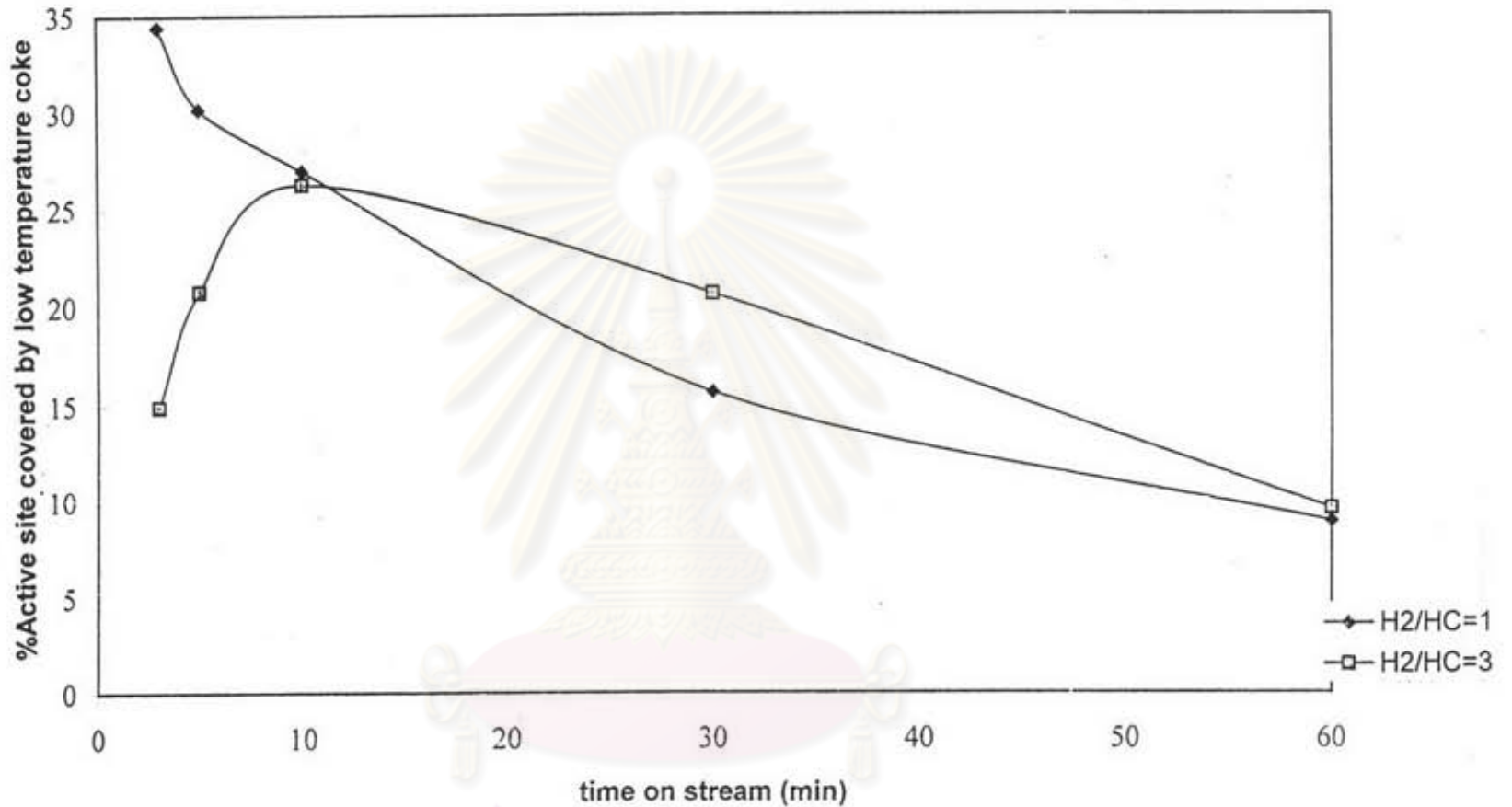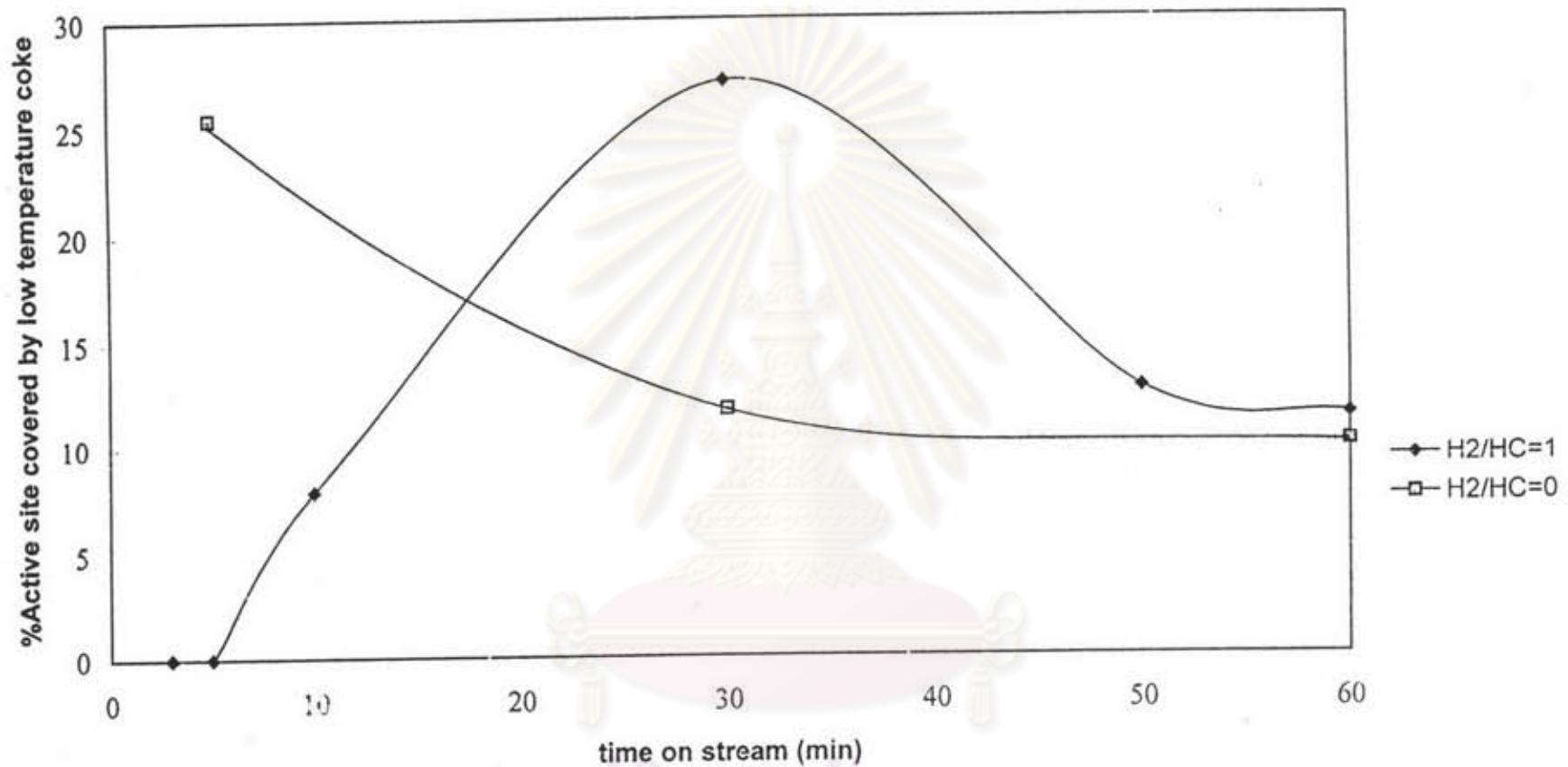
Figure 5.10 %Active site covered by low temperature coke of Pt/Al$_2$O$_3$ at reaction temperature 500 °C, GHSV=22,525 hr^{-1}, 20%propane in N$_2$ balance regeneration temperature 200 °C

Figure 5.11 %Active site covered by low temperature coke of Pt-Sn/Al$_2$O$_3$ at reaction temperature 500 $^\circ$C, GHSV=22,525 hr^{-1} ,20%propane in N$_2$ balance, regeneration temperature 200 $^\circ$C
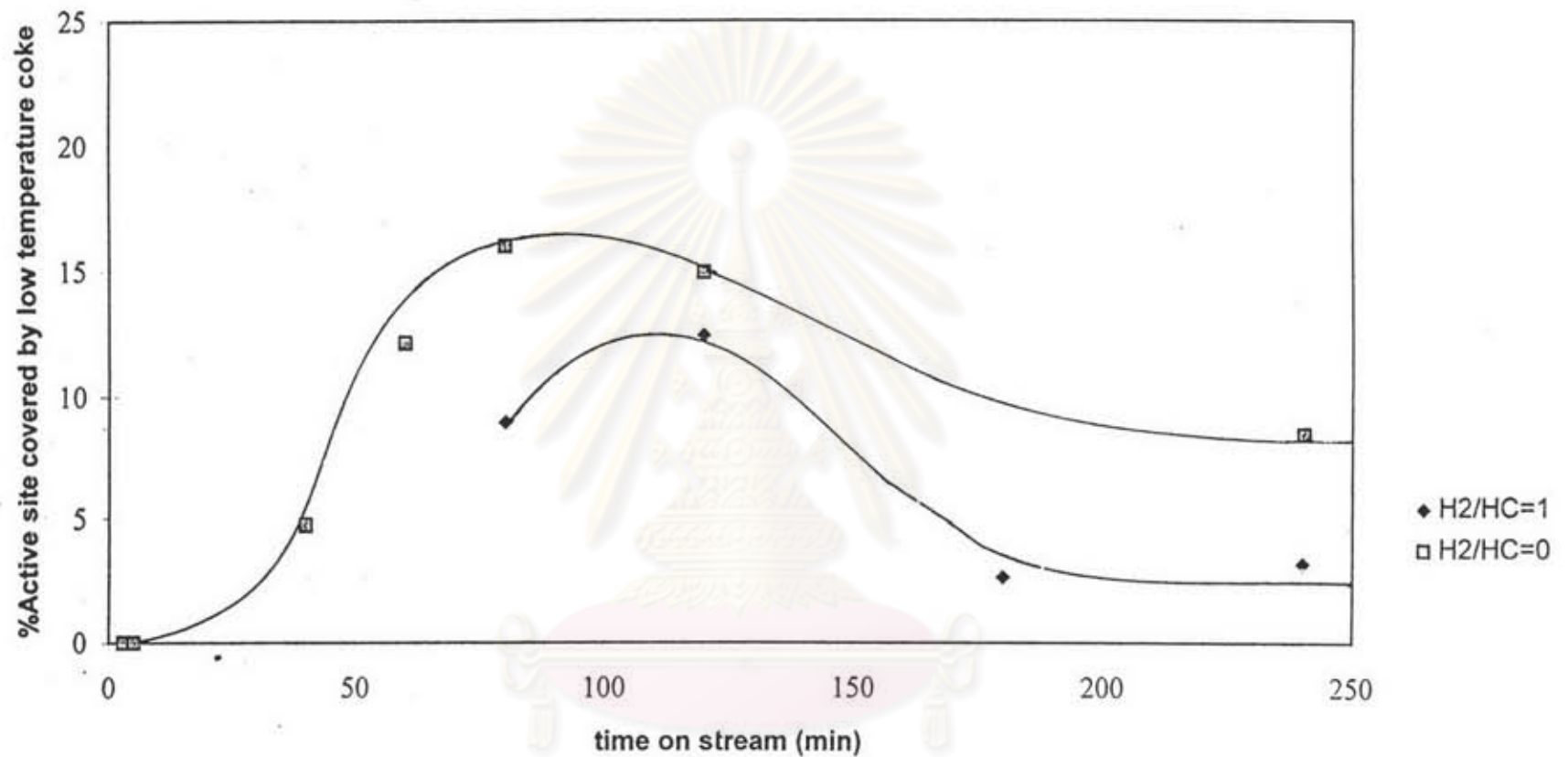
Figure 5.12 %Active site covered by low temperature coke of Pt-Sn-K/Al$_2$O$_3$ at reaction
temperature 500 °C, GHSV=22,525 hr^{-1} ,20%propane in N$_2$ balance,
regeneration temperature 200 °C

maximum value is shifted to the longer time on stream. Therefore, Pt-Sn-K/Al_2O_3 better withstands more low temperature coke deposit on metal active sites by delay its formation to longer time on stream than Pt-Sn/Al_2O_3 and Pt/Al_2O_3.

The shifting of low temperature coke to longer time on stream on metal active site of Pt-Sn and Pt-Sn-K catalyst when adding hydrogen to feed stream can be postulated to the principle of Le Chatelier. Low temperature coke is produced from coke precursor by dehydrogenation. Thus, introduction of hydrogen to feed stream reduces coke precursor. Then, low temperature coke formation on metal active site is delayed.

Consideration to asymptote value of metal active sites covered by low temperature coke of Pt and Pt-Sn catalysts for both case of H2/HC=0 and H2/HC=1 a similar value is obtained. Hence, Sn does not decrease the amount of low temperature coke deposit on metal active sites. However, added Sn delays low temperature coke deposit on metal active sites to longer time on stream.

Metal active site covered by low temperature coke at asymptote of Pt-Sn-K catalyst for H_2/HC=0 is slightly less than Pt and Pt-Sn catalyst. But in the condition H_2/HC=1 metal active site covered by low temperature coke of Pt-Sn-K is obviously decreased. The model which describe these phenomena is proposed as follow.
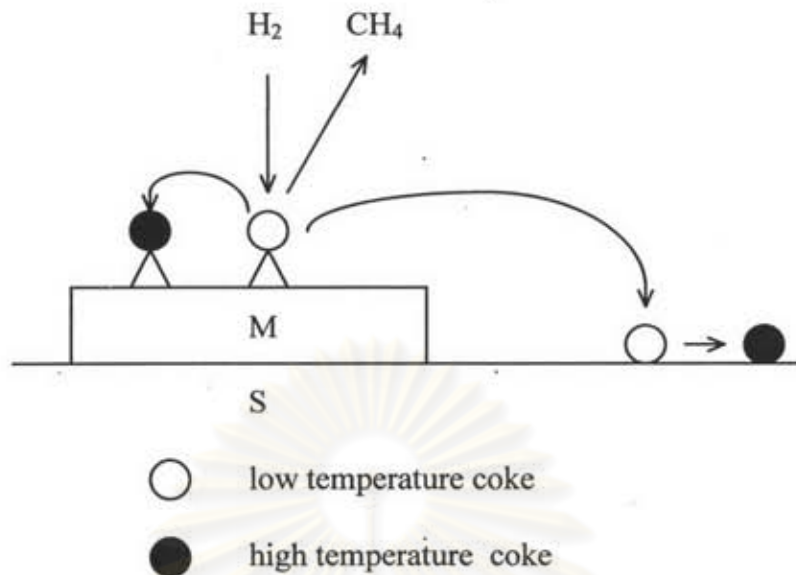
Figure 5.13 Proposed model for low temperature coke deposition on metal active site

At asymptote or pseudo steady-state rate of low temperature coke accumulation = 0. Then,

rate of low temperature coke generation = rate of hydrogasification + rate of

transformation to high temperature coke + rate of drain off to support.

Rate of transformation to high temperature coke is constant at asymptote and it depend on the amount of low temperature coke. Therefore, it has less effect on the low temperature coke.

Finally, rate of low temperature coke generation = rate of   hydrogasification

+ rate of drain off to support.

Thus, the decrease of low temperature coke on metal active site of Pt-Sn-K catalyst is due to hydrogasification and drain off. When hydrogen is added to feed stream, metal active site covered by low temperature coke is decreased. So, it can be postulated that

the main factor which reduce low temperature coke on metal active site is hydrogasification.