CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Preparation

The catalysts prepared in this work are listed in Table 4.1. In catalyst preparation, it was observed that the difference in color of catalyst preparation with different composition and order of impregnation, the calcined catalysts gave different colors. In particular, all Pt catalysts had a yellowish color, similar to the color of Pt impregnating solution. Pd/Al_2O_3 and $PtPd/Al_2O_3$ catalysts had an orange color, similar to the color of the precursor solutions. By contrast, the $Pt-F/Al_2O_3$ and $PtPd-F/Al_2O_3$ became grey after calcinations and $Pd-F/Al_2O_3$ became darker in color than the F-unpromoted catalysts. Moreover, they were not homogeneous and exhibited different degree of darkness, even within the same pallet. In addition, the $F-Pt/Al_2O_3$, $F-Pd/Al_2O_3$ and $F-PtPd/Al_2O_3$ catalysts in which F was added after were darker in color than the ones prepared by adding F before metals.

4.2 Catalyst Characterization

4.2.1 Temperature Programmed Reduction (TPR)

This technique allows getting information about the interaction of the metal components by means of the measurement of the hydrogen consumption during the reduction of the oxides at a constant heating rate. The temperature at which reduction occurs and the number and position of reduction peaks depend on oxidation state of the metals, interaction of the oxides among them, interaction of the oxides to catalyst, and catalytic action of neighbor metal present or generated during reduction (Carvalho *et al.*, 2004). From the TPR profile, it was seen that each metal exhibited different reduction temperatures. From Figure 4.1, TPR profiles of Pt/Al_2O_3, the presence of three reduction peaks in the TPR curves was inferred. The low-temperature peak at 100°C corresponds to the reduction of PtO_2 species (Borgna *et al.*, 1999). The middle temperature peak, a maximum temperature peak at about 220°C, arises from the reduction of oxy- or hydroxychlorinated Pt species in the

three-dimensional bulk phase (Navarro *et al.*, 2005). At high temperatures, the hydrogen consumption peak is the reduction of oxychlorinated species in two-dimensional dispersive phase, with a strong interaction with alumina (Hwang and Yeh, 1996). Thus, only the low and middle temperature peaks are related to the reduction of oxidized Pt species. For the F-promoted catalyst prepared with different order of impregnating between Pt and F present different peaks from the Pt without F as shown in Figure 4.1. The TPR profile of Pt-F/Al$_2$O$_3$ (added F before Pt) had a dominant peak more than F-Pt/Al$_2$O$_3$ (added Pt before F), may be because F precursor could reduce in the calcination step. Thus, from Figure 4.1 the hydrogen consumption at 220°C of Pt catalyst is prominent. The total hydrogen consumption corresponds to the total reduction of Pt (IV) to Pt (0) (Mazzieri *et al.*, 2005). The negative peak of hydrogen desorption for F-Pt/Al$_2$O$_3$ catalysts, could be because part of metal had been reduced during calcination of F precursor and when flow hydrogen onto the surface of catalyst at room temperature the hydrogen can reduce more easier than the F-unpromoted Pt catalyst, so when heat up the F-promoted catalyst the hydrogen on the surface can be desorbed more easier than the F-unpromoted catalyst.
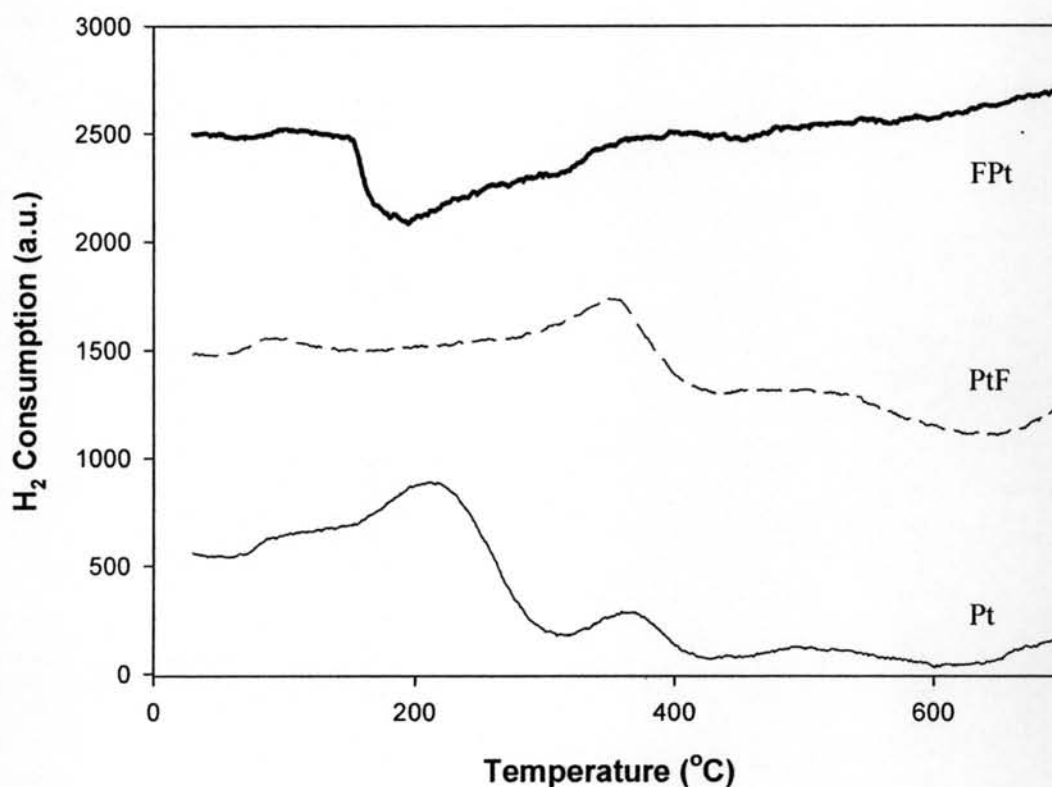
Figure 4.1 TPR profiles of Pt/Al$_2$O$_3$, PtF/Al$_2$O$_3$ and FPt/Al$_2$O$_3$ catalyst.

From Figure 4.2, the TPR profiles of the Pd sample shows a positive peak at 100°C which is the reduction of PdO species. The TPR profile of Pd sample shows a broad reduction peak which suggested the presence of several Pd species. May be a small amount of chlorine could still present in the calcined Pd/Al$_2$O$_3$ catalyst. It may be concluded that the PdO could still present on the sample. For the order of impregnation between Pd and F, The TPR profile of PdF/Al$_2$O$_3$ (added F before Pd) had a dominant peak more than FPd/Al$_2$O$_3$ (added Pd before F), may be because F precursor could reduce in the calcination step. Moreover, the addition of F after Pd shows a negative peak at 120 °C due to the β-PdH$_x$ decomposition which is formed by the reduction of PdCl$_2$ (Fig. 4.2).
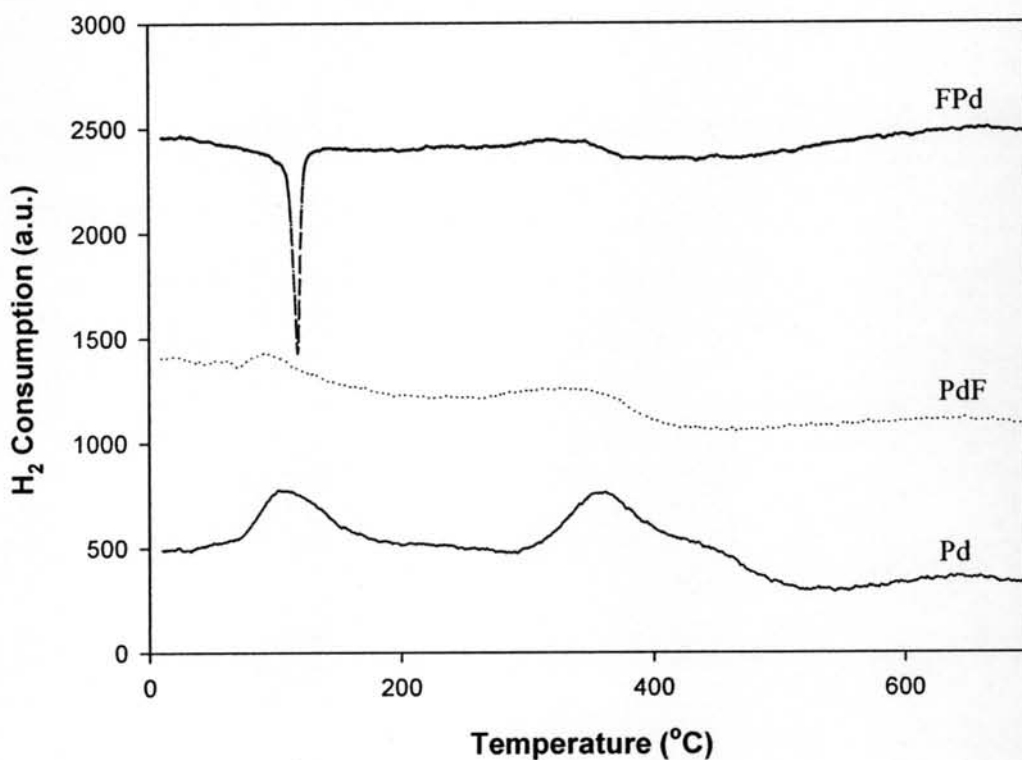
Figure 4.2 TPR profiles of Pd/Al$_2$O$_3$, PdF/Al$_2$O$_3$ and FPd/Al$_2$O$_3$ catalyst.

The TPR profile of the bimetallic PtPd catalyst could not be explained by the simple addition of the individual contribution of the two metals, implying some kind of interaction between the metallic particles (Kim *et al.*, 2003). The bimetallic PtPd catalyst (Figures 4.3) shows an important main reduction zone with a maximum at 150°C in the region that occurs the Pd reduction in the monometallic catalyst. The decrease in hydrogen consumption associated with the PdO species seemed to depend on the presence of Pt. The reduction of PtPd without F-promoter seemed to be different from the PtPd with F-promoter because the PtPd without F-promoter give higher hydrogen consumption than PtPd with F-promoter that because of metal had been reduced during calcination of F precursor which were shown in Figures 4.3.
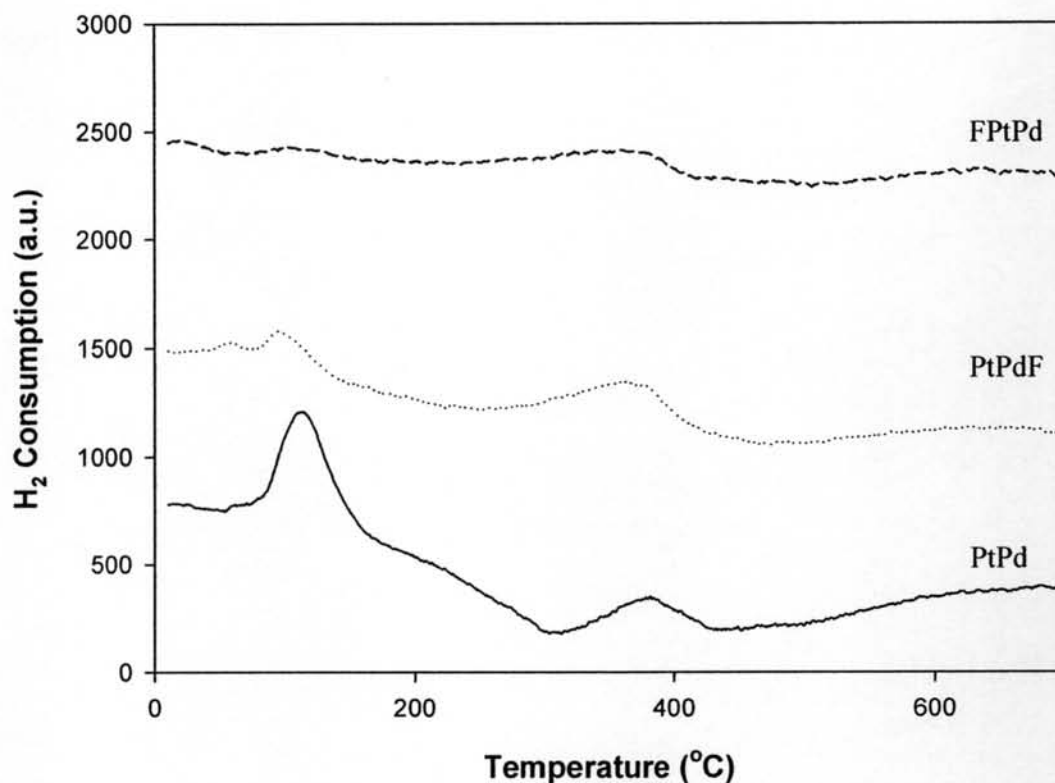
Figure 4.3 TPR profiles of PtPd/Al$_2$O$_3$, PtPdF/Al$_2$O$_3$ and FPtPd/Al$_2$O$_3$ catalyst.

However, TPR analysis is not enough to conclude the effect of the order of impregnation on the catalytic activity. To be explained the effect of the order of impregnation, other characterization techniques, such as hydrogen chemisorption, X-ray photoelectron spectroscopy (XPS) and Atomic adsorption spectroscopy (AAS), are also investigated.

4.2.2 <u>Hydrogen Chemisorption</u>

Hydrogen chemisorption is a technique for determining metal dispersion of the catalyst. The percentage dispersion degree, adsorbing metal atoms to total metal atoms, was calculated based on the mole of hydrogen chemisorbed on the metal in the catalyst. The results were illustrated in Table 4.2. From the experiments, the addition of F-promoter gave the lower metal dispersion than un-promoted for all catalyst. For the order of impregnation, the addition of F before the metal give lower metal dispersion than the addition of F after the metal in Pt catalyst

but not for Pd and PtPd catalyst. Since, fluorinated aluminas are more hydrophobic and tend to lose surface area more easily than the parent alumina supports. These changes seem to be adversely affecting the metal dispersion during the calcinations (Ghosh and Kydd, 1985).

Table 4.1 List of the dispersion degree (%) of Pt, Pd, and PtPd catalyst with and without F-promoter which calcined at 500°C

Catalyst	Calcination temperature (°C)	Metal dispersion (H/M)
Pt/Al$_2$O$_3$	500	70.14
Pt-F/Al$_2$O$_3$	500	19.64
F-Pt/Al$_2$O$_3$	500	38.49
Pd/Al$_2$O$_3$	500	62.97
Pd-F/Al$_2$O$_3$	500	57.43
F-Pd/Al$_2$O$_3$	500	53.82
Pt-Pd/Al$_2$O$_3$	500	58.83
PtPd-F/Al$_2$O$_3$	500	51.58
F-PtPd/Al$_2$O$_3$	500	49.87

4.2.3 X-ray Photoelectron Spectroscopy (XPS)

The atomic surface compositions of the calcined Pd and Pt-Pd catalysts were analyzed by an X-ray photoelectron as shown in Table 4.3. It can be seen that the oxygen concentration decreased with the addition of F because the incorporation of F replaces O or OH of the oxide catalysts. Noticeably, the concentration of residual Cl on the surface, from the metal precursors, was reduced when F was added.

Table 4.2 Atomic surface composition (mol%) of different catalysts which calcined at 500°C obtained by XPS analysis

Catalyst 500°C	O1s	F1s	Al2p	Cl2p	Pd3d
Pd/Al$_2$O$_3$	0.489	0.000	0.498	0.011	0.001
Pd/F-Al$_2$O$_3$	0.475	0.033	0.466	0.006	0.003
F-Pd/Al$_2$O$_3$	0.464	0.043	0.489	0.003	0.001
Pt-Pd/Al$_2$O$_3$	0.494	0.000	0.497	0.006	0.003
Pt-Pd/F-Al$_2$O$_3$	0.455	0.051	0.489	0.003	0.002
F-Pt-Pd/Al$_2$O$_3$	0.465	0.032	0.497	0.004	0.002

4.2.4 Atomic Adsorption Spectroscopy (AAS)

Atomic adsorption spectroscopy was used to determine the actual contents of Platinum (Pt) and Palladium (Pd) loadings in the prepared catalysts as shown in Table 4.4.

Table 4.3 Chemical composition of the catalysts determined by AAS

Catalyst	Calculated value (%wt)		Actual value (%wt)	
	Pt	Pd	Pt	Pd
Pt/Al$_2$O$_3$	1.6	-	1.87	-
PtF/Al$_2$O$_3$	1.6	-	1.69	-
FPt/Al$_2$O$_3$	1.6	-	1.68	-
Pd/Al$_2$O$_3$	-	0.8	-	0.96
PdF/Al$_2$O$_3$	-	0.8	-	0.99
FPd/Al$_2$O$_3$	-	0.8	-	0.91
PtPd/Al$_2$O$_3$	0.4	0.6	0.64	0.75

Table 4.3 (Continued)

Catalyst	Calculated value (%wt)		Actual value (%wt)	
	Pt	Pd	Pt	Pd
PtPdF/Al$_2$O$_3$	0.4	0.6	0.59	0.74
FPtPd/Al$_2$O$_3$	0.4	0.6	0.57	0.61

4.3 Catalytic Activity Testing

4.3.1 Hydrogenation of Tetralin

The tetralin hydrogenation was carried out at temperature of 300°C with a constant total pressure of 500 psig and a constant hydrogen/hydrocarbon molar feed ratio of 11 under free sulfur. Only two main products, *trans-* and *cis-*decalin, were found under this condition. Although the hydrogenation of aromatic compounds is generally considered as the reversible reactions (Spare and Gates, 1981), the small amount of dehydrogenation product, naphthalene, was found over the condition of this study. Therefore, the dehydrogenation reaction could be neglected. Based on the reaction products, tetralin hydrogenation can be described by these three reactions:

tetralin + 3H$_2$ $\xrightarrow{k_1}$ cis-decalin   (4.1)

tetralin + 3H$_2$ $\xrightarrow{k_2}$ trans-decalin   (4.2)

cis-decalin $\underset{k_3^-}{\overset{k_3}{\rightleftharpoons}}$ trans-decalin   (4.3)
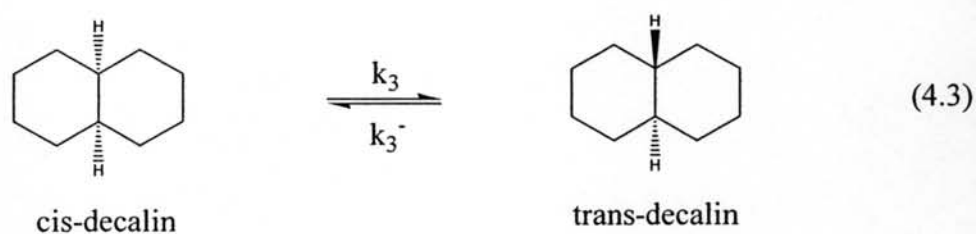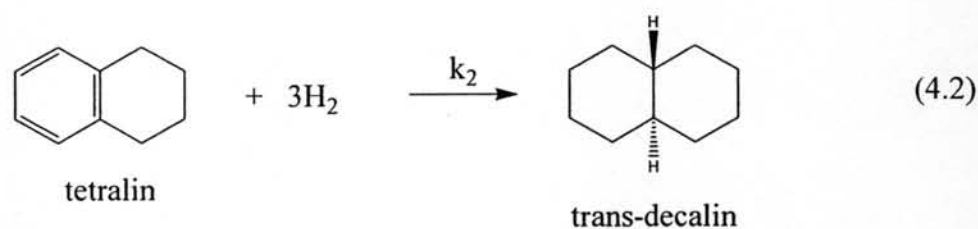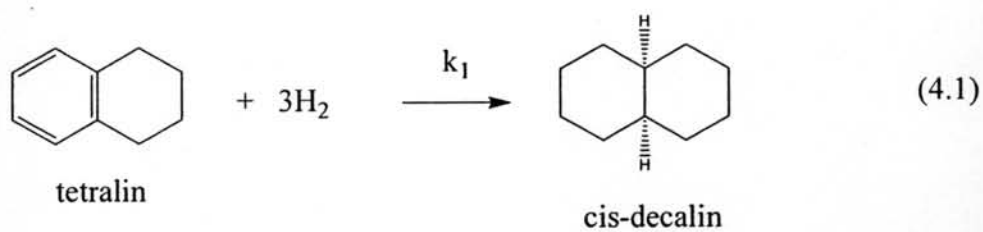
These reactions were also proposed by Weitkamp (1968). The first two reactions are the hydrogenation of tetralin to *cis-* and *trans*-decalin, respectively. Due to the high total pressure and hydrogen/hydrocarbon molar feed ratio, the hydrogenations of tetralin are considered irreversible. The last reaction is the reversible isomerization of *cis-* and *trans*-decalin. This reaction was taken place at high conversion of tetralin (Jongpatiwut *et al.*, 2004).
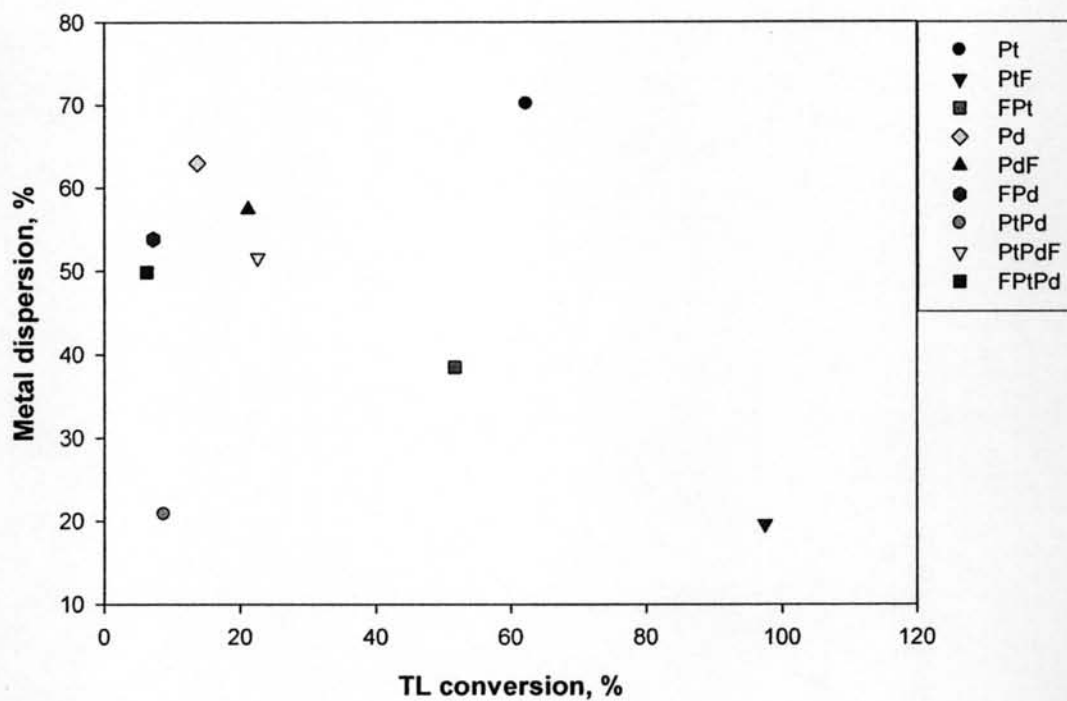
Figure 4.4 The overview of metal dispersion and conversion among catalysts.

Figure 4.4 shows the metal dispersion among catalysts with different order of impregnation depended on the intrinsic properties of the metal. Particularly, Pt metal had very high dispersion and high catalytic activity.
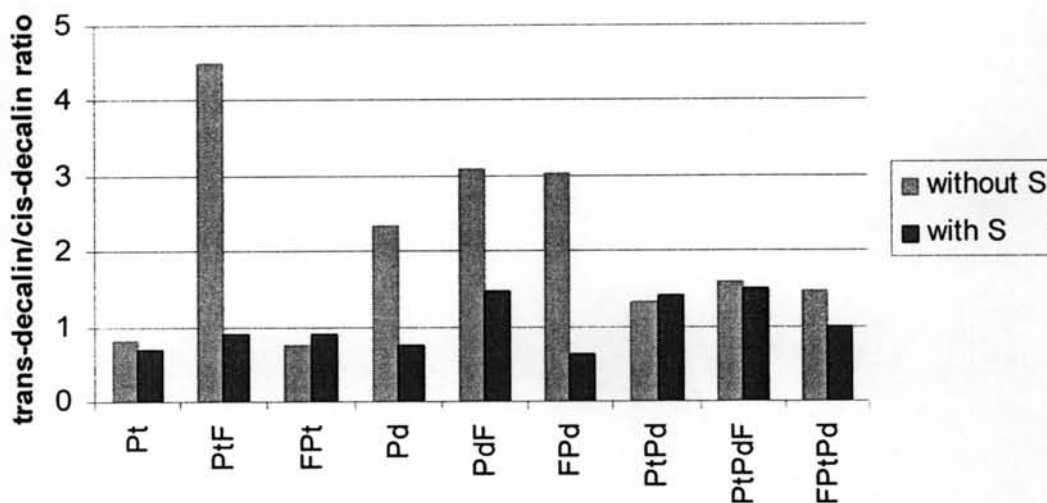
Figure 4.5 Effect of sulfur in the feed stock and F-promoted support on the tetralin hydrogenation selectivity for different catalysts.

Figure 4.5 shows the trans-decalin/cis-decalin ratio in tetralin hydrogenation over monometallic Pt and Pd, and the bimetallic catalysts with and without F. As for the PtPd catalyst, presence of sulfur (electron withdrawing) as well as the sulfur free had little effect on the trans-decalin/cis-decalin ratio. This suggests that the electric properties of the hydrogenation active sites over the bimetallic PtPd particles were less influenced by sulfur during the HYD reaction. For monometallic catalyst Pd metals favored trans-decalin formation to a greater extent than Pt metals. The trans-decalin/cis-decalin ratio indicated that Pd properties were dominant in the bimetallic PtPd particles. On the other hand, for the PtPd catalysts, presence of sulfur decrease the trans-decalin/cis decalin ratio significantly, similar to the monometallic Pd catalysts (Yoshimura *et al.*, 2007).

Table 4.5 presents conversions of Pt, Pd, and PtPd with and without F-promoter supported on γ-Al_2O_3 in the hydrogenation of tetralin under free sulfur. The order of impregnating between Pt and F-promoter had affected on tetralin conversion, as a result added F before Pt (Pt-F/Al_2O_3) can enhance the tetralin conversion more than added Pt before F (F-Pt/Al_2O_3). Moreover, the addition of F

after the metal (F-Pt/Al$_2$O$_3$) give a lower tetralin conversion than unpromoted catalyst that can be because F precursor could reduce in the calcination step and when catalyst was reduced and calcined in the same time it can cause the agglomeration of metal catalysts. And for the addition F before Pt (Pt-F/Al$_2$O$_3$) which can enhance the tetralin conversion more the F-unpromoted catalyst can be because the F-promoted catalyst has the electron deficient more than the F-unpromoted catalyst so it can cause aromatic (high electron density) more easier to adsorb on the surface. As a result, it enhance the tetralin conversion of the the addition F before Pt. On the other hand, the conversion of Pd and PtPd/Al$_2$O$_3$ was lower than Pt due to the intrinsic properties of Pd. The conversion of PtPd/Al$_2$O$_3$ was not significantly different from Pd because of Pd covering above Pt (Yasuda *et al.*, 1999). Therefore, the behavior of PtPd was similar to Pd.

Table 4.4 List of conversions of Pt, Pd, and PtPd with and without F-promoter

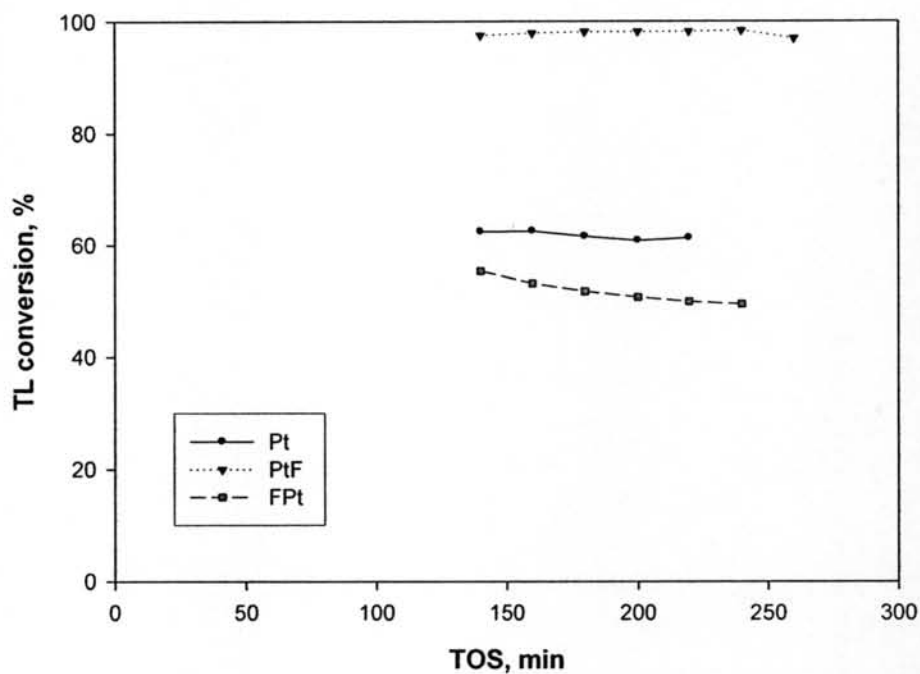| Catalyst	Calcination temperature (°C)	TL conversion (%)	Metal dispersion (H/M)
Pt/Al$_2$O$_3$	500	62.28	70.14
Pt-F/Al$_2$O$_3$	500	97.47	19.64
F-Pt/Al$_2$O$_3$	500	51.71	38.49
Pd/Al$_2$O$_3$	500	13.72	62.97
Pd-F/Al$_2$O$_3$	500	21.17	57.43
F-Pd/Al$_2$O$_3$	500	7.17	53.82
Pt-Pd/Al$_2$O$_3$	500	8.76	58.83
PtPd-F/Al$_2$O$_3$	500	22.60	51.58
F-PtPd/Al$_2$O$_3$	500	6.23	49.87

Figure 4.6 Conversion of tetralin as a function of time on stream (TOS) over Pt catalyst. Reaction condition: 500 psig, 300°C, $H_2/HC=11$.
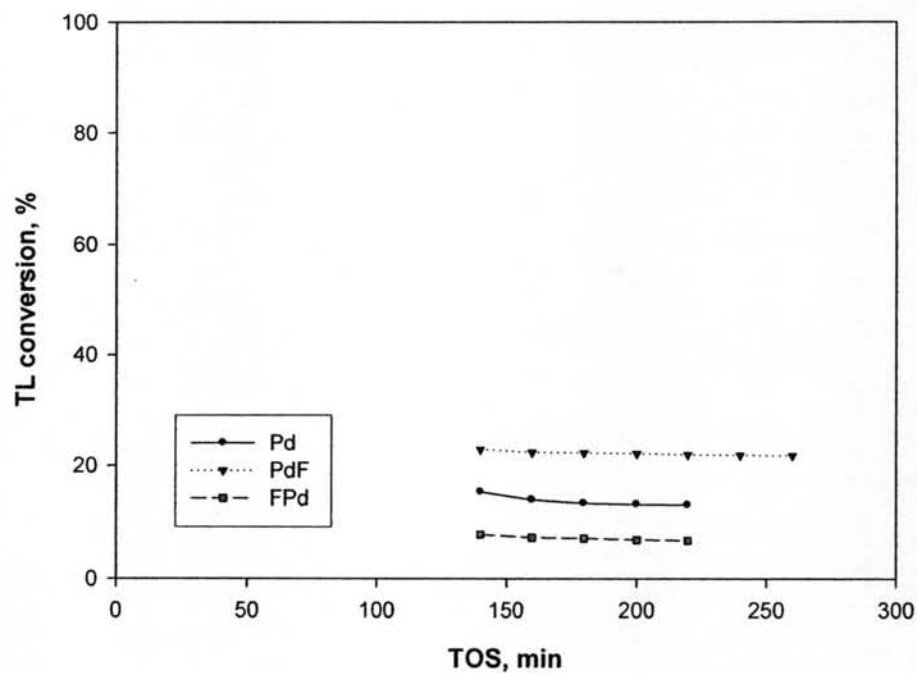

Figure 4.7 Conversion of tetralin as a function of time on stream (TOS) over Pd catalyst. Reaction condition: 500 psig, 300°C, $H_2/HC=11$.
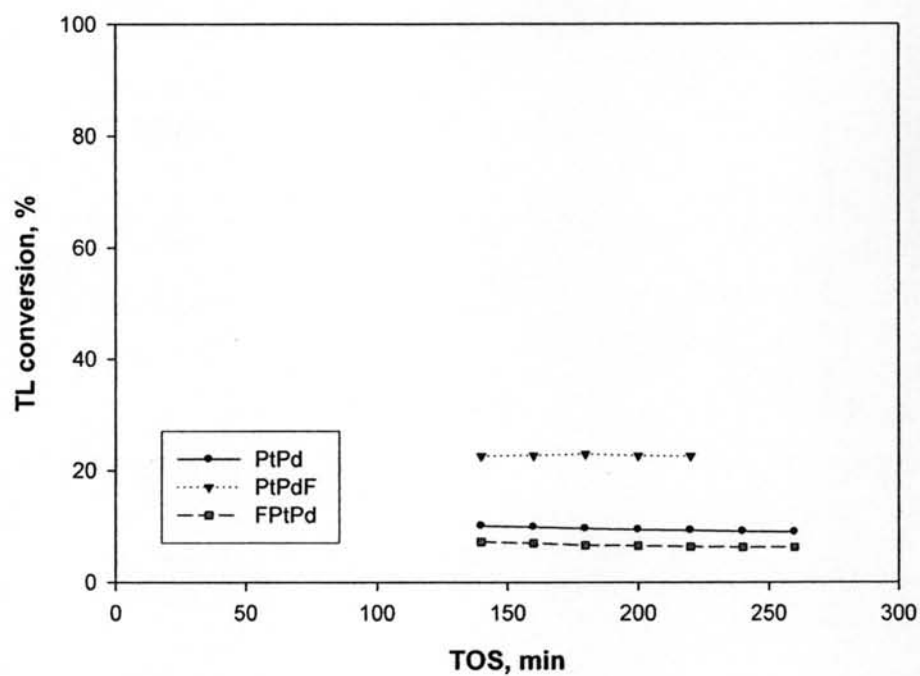
Figure 4.8 Conversion of tetralin as a function of time on stream (TOS) over PtPd catalyst. Reaction condition: 500 psig, 300°C, H_2/HC=11.
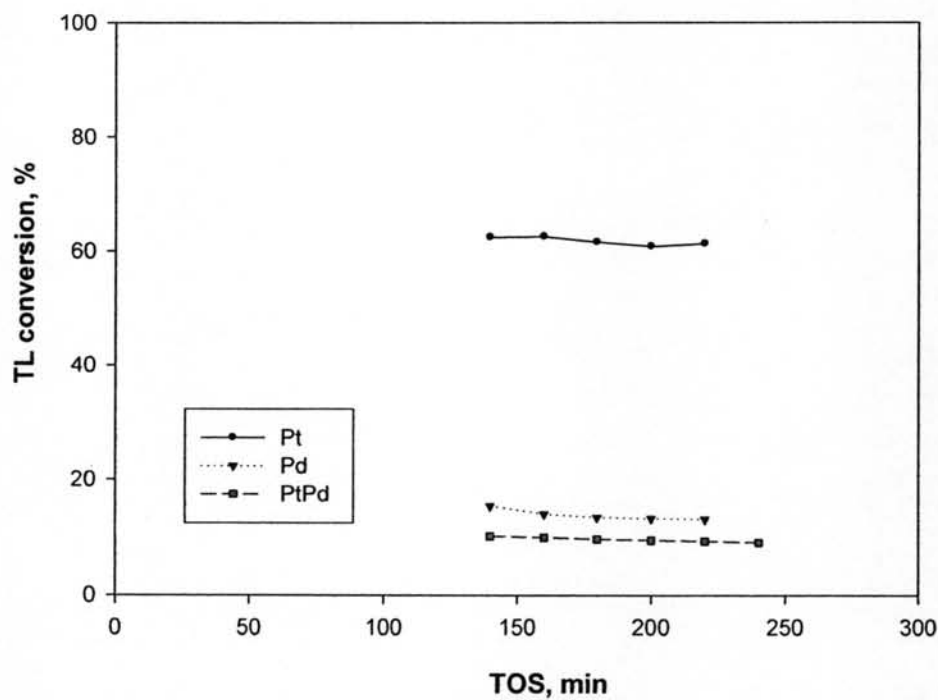

Figure 4.9 Conversion of tetralin as a function of time on stream (TOS) over Pt, Pd and PtPd catalyst. Reaction condition: 500 psig, 300°C, H_2/HC=11.

4.3.2 Inhibition of Hydrogenation Activity by Sulfur Compounds

The effect of sulfur on the catalytic activity was tested by using the dodecane as a diluent in the dodecane:tetralin ratio of 75:25 and containing 350 ppm S. From Figure 4.10, the conversion of Pt, Pd and PtPd catalyst decreased with time on stream when DBT was present in the feed, but the degree of deactivation significantly differed among the catalysts. PtPd catalyst showed a small deactivation and slightly different in conversion with Pt catalyst. Pd catalyst showed a low conversion even at the initial stage of the reaction.
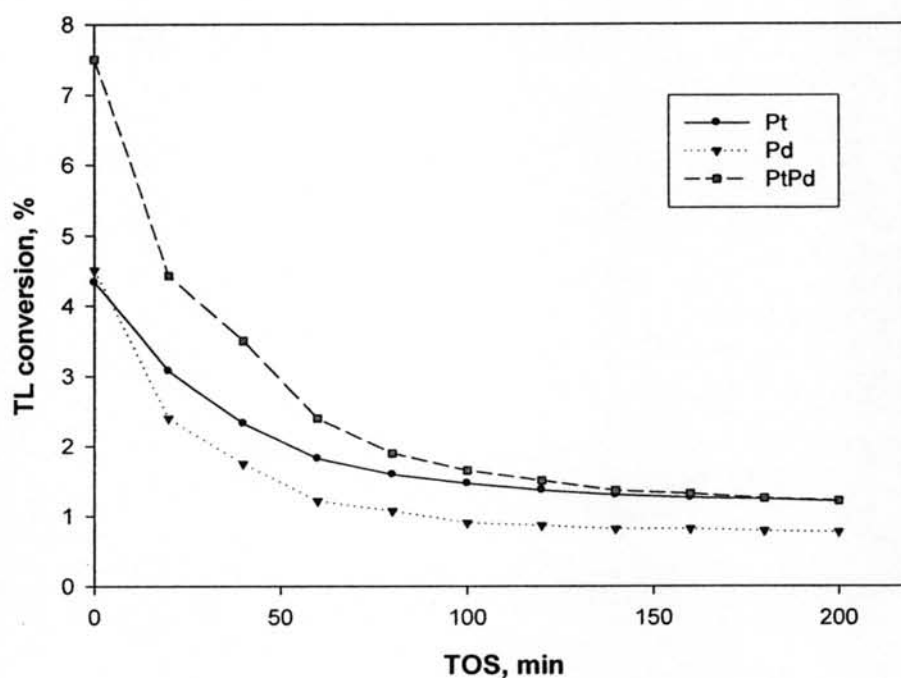

Figure 4.10 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over Pt, Pd and PtPd catalyst. Reaction condition: 500 psig, 300°C, $H_2/HC=11$.

The addition of fluorine has the effect of increasing the sulfur tolerance of all catalysts that can be due to the addition of F to the catalysts increases the amounts of both acid sites but the Bronsted sited are increased to a greater extent (Kim *et al.*, 2003) and from the previous work (Hu *et al.*, 2001) showed that strong Bronsted acidic sites would promoted the sulfur resistance of supported Pt, Pd and PtPd catalyst, while Lewis acidic sites do not. For the Pt catalyst as shown in Figure 4.11

was found that the addition of F before the metal give a higher sulfur tolerance than the addition of F after the metal for all catalysts as shown in Figures 4.11, 4.12 and 4.13, respectively.
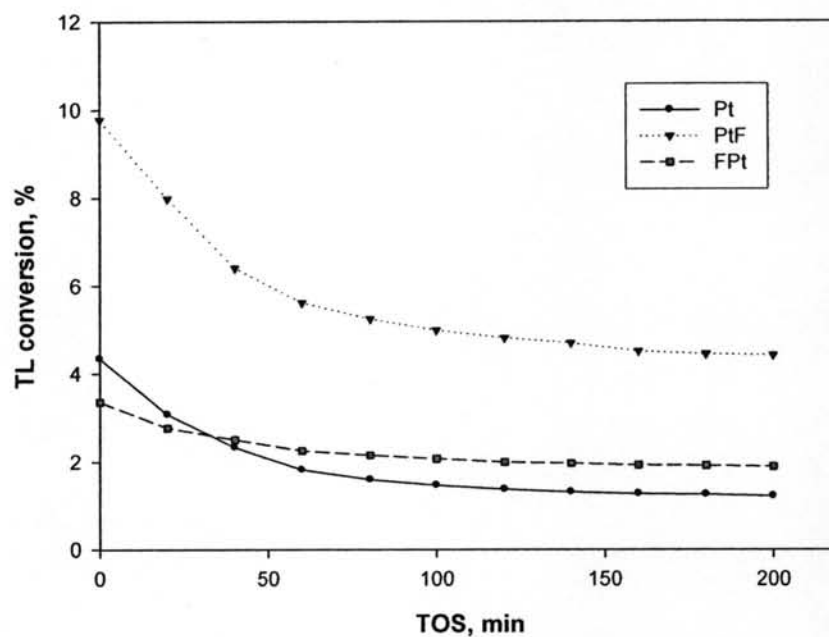

Figure 4.11 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over Pt catalyst. Reaction condition: 500 psig, 300°C, $H_2/HC=11$.
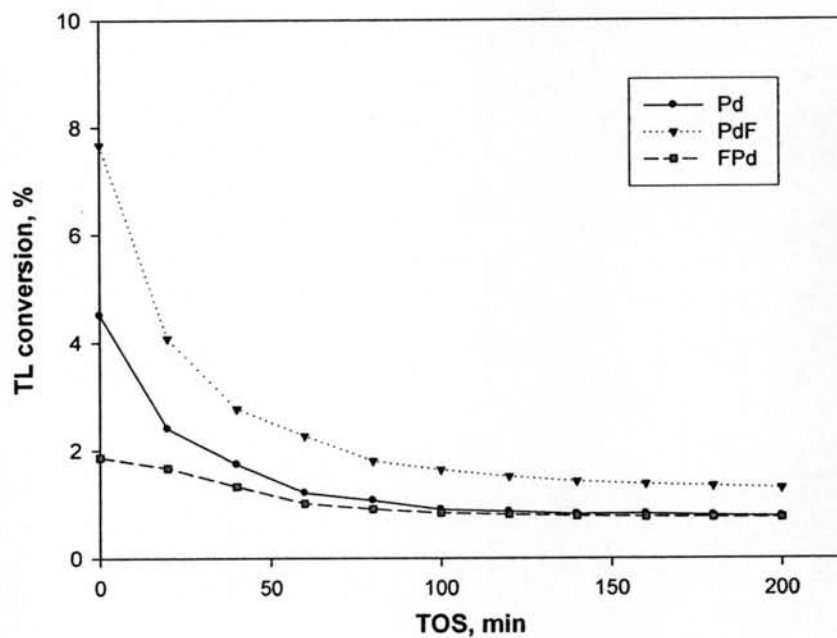
Figure 4.12 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over Pd catalyst. Reaction condition: 500 psig, 300°C, $H_2/HC=11$.
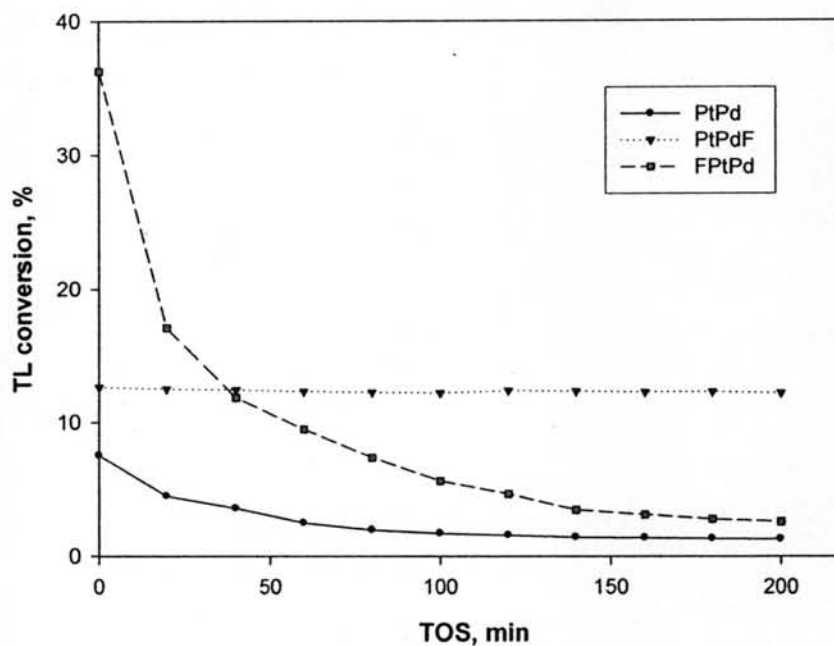

Figure 4.13 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over PtPd catalyst. Reaction condition: 500 psig, 300°C, $H_2/HC=11$.