

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Preparation

The catalysts prepared with different conditions are listed in Table 4.1. In catalyst preparation, it was observed that the different composition and the order of impregnation gave different colors. In particular, all Pt catalysts had a yellowish color, similar to the color of Pt impregnating solution. Pd/Al₂O₃ and PtPd/Al₂O₃ catalysts had an orange color, similar to the color of the precursor solutions. By contrast, the addition of F, the Pt-F/Al₂O₃, Pd-F/Al₂O₃ and PtPd-F/Al₂O₃ became grey after calcinations. Moreover, they were not homogeneous and exhibited different degree of darkness, even within the same pellet. In addition, the F-Pt/Al₂O₃, F-Pd/Al₂O₃ and F-PtPd/Al₂O₃ catalysts in which F was added after metal were darker in color than the ones prepared by adding F before metals. This is because the presence of F precursor could partially reduce the metals in calcination step. This evidence will be further discussed in TPR section.

Table 4.1 List of prepared catalysts

Catalyst	Calcination temperature (°C)	Pt loading (%)	Pd loading (%)	F loading (%)	Order of impregnation
Pt/Al ₂ O ₃	250	1.6	-	-	Pt
Pt/Al ₂ O ₃	300	1.6	-	-	Pt
Pt/Al ₂ O ₃	350	1.6	-	-	Pt
Pd/Al ₂ O ₃	250	-	0.8	-	Pd
Pd/Al ₂ O ₃	300	-	0.8	-	Pd
Pd/Al ₂ O ₃	350	-	0.8	-	Pd
Pt-Pd/Al ₂ O ₃	250	0.4	0.6	-	PtPd
Pt-Pd/Al ₂ O ₃	300	0.4	0.6	-	PtPd
Pt-Pd/Al ₂ O ₃	350	0.4	0.6	-	PtPd
F-Pt/Al ₂ O ₃	250	1.6	-	3.0	Pt, F
F-Pt/Al ₂ O ₃	300	1.6	-	3.0	Pt, F
F-Pt/Al ₂ O ₃	350	1.6	-	3.0	Pt, F

Table 4.1 List of prepared catalysts (Cont.)

Catalyst	Calcination temperature (°C)	Pt loading (%)	Pd loading (%)	F loading (%)	Order of impregnation
Pt-F/Al ₂ O ₃	250	1.6	-	3.0	F, Pt
Pt-F/Al ₂ O ₃	300	1.6	-	3.0	F, Pt
Pt-F/Al ₂ O ₃	350	1.5	-	3.0	F, Pt
F-Pd/Al ₂ O ₃	250	-	0.8	3.0	Pd, F
F-Pd/Al ₂ O ₃	300	-	0.8	3.0	Pd, F
F-Pd/Al ₂ O ₃	350	-	0.8	3.0	Pd, F
Pd-F/Al ₂ O ₃	250	-	0.8	3.0	F, Pd
Pd-F/Al ₂ O ₃	300	-	0.8	3.0	F, Pd
Pd-F/Al ₂ O ₃	350	-	0.8	3.0	F, Pd
F-PtPd/Al ₂ O ₃	250	0.4	0.6	3.0	PtPd, F
F-PtPd/Al ₂ O ₃	300	0.4	0.6	3.0	PtPd, F
F-PtPd/Al ₂ O ₃	350	0.4	0.6	3.0	PtPd, F
PtPd-F/Al ₂ O ₃	250	0.4	0.6	3.0	F, PtPd
PtPd-F/Al ₂ O ₃	300	0.4	0.6	3.0	F, PtPd
PtPd-F/Al ₂ O ₃	350	0.4	0.6	3.0	F, PtPd

4.2 Catalyst Characterization

4.2.1 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) was utilized to determine the temperature at which metal precursor is decomposed in an ambient air. In Figures 4.1, 4.2 and 4.3, the decomposition temperature of Pt precursor was decomposed at 250°C while the decomposition temperature of Pd and PtPd precursors was decomposed at 230°C. However, the weight of sample keeps decreasing as a function of temperature it might be due to the oxidation of oxychlorinated compound that strongly adsorbed to the surface. In addition, the use of chlorinated platinum precursors for complete oxidation reactions has resulted in several problems due to the reported inhibition effect and its elimination during the reduction itself (Paulis *et al.*, 2001). In this work, the calcination temperature at least 250°C is selected to make sure that each metal precursor can be decomposed at that calcination temperature.

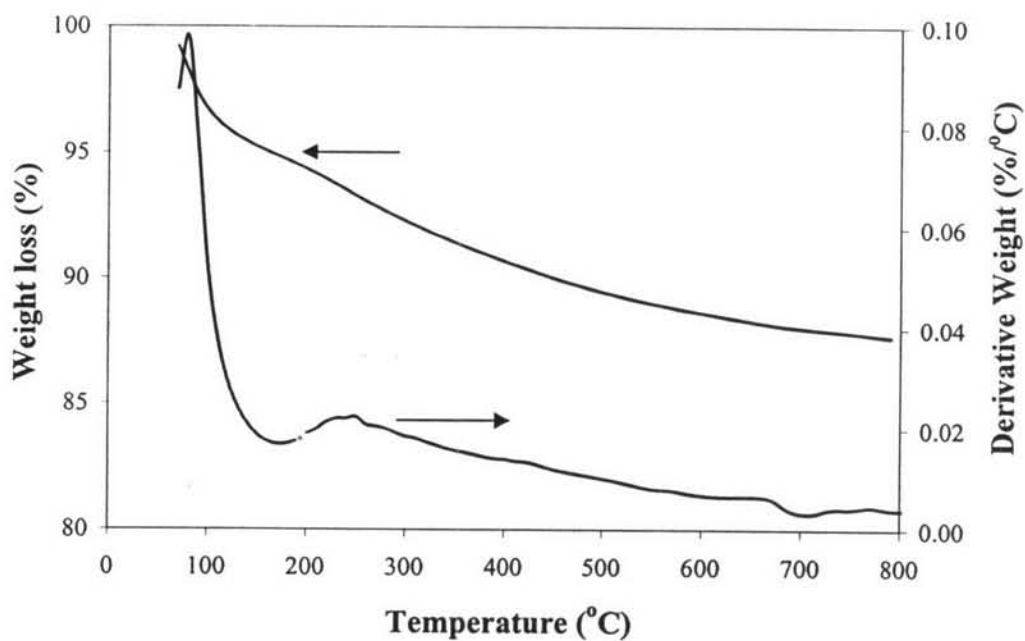


Figure 4.1 TGA profile of Pt/Al₂O₃ as a function of temperature.

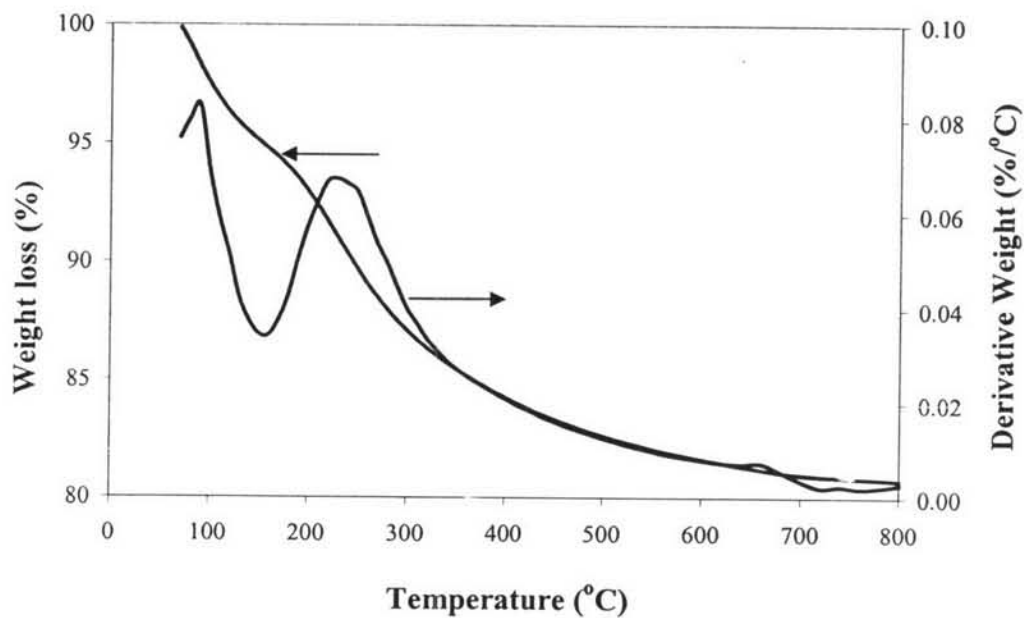


Figure 4.2 TGA profile of Pd/Al₂O₃ as a function of temperature.

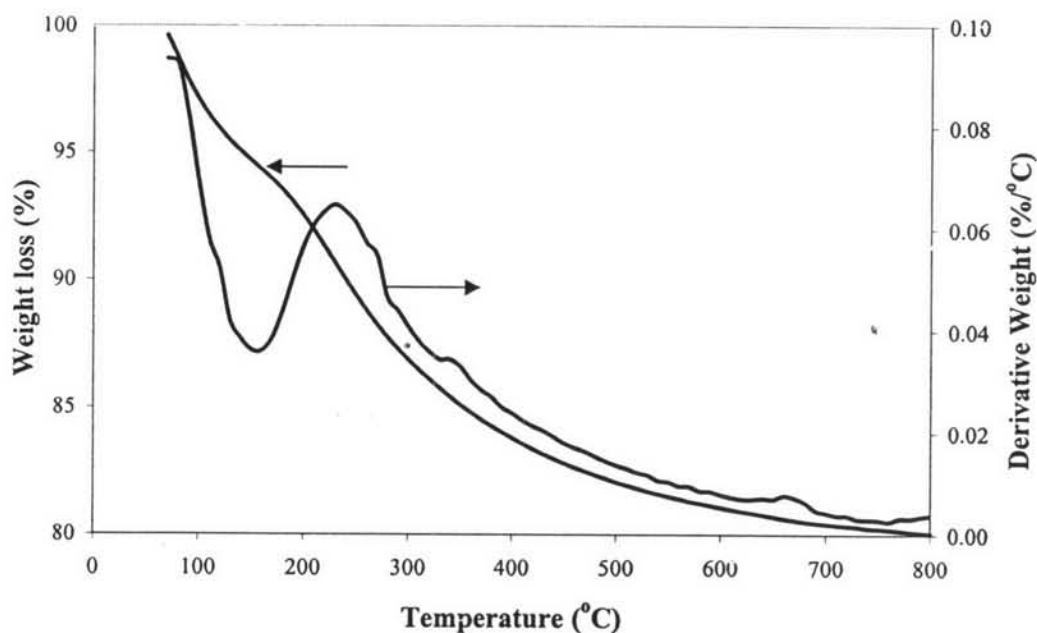


Figure 4.3 TGA profile of PtPd/Al₂O₃ as a function of temperature.

4.2.2 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 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 4.4, TPR profiles of Pt/Al₂O₃, the presence of three reduction peaks in the TPR curves was inferred. The low-temperature peak corresponds to the reduction of PtO₂ species (Borgna *et al.*, 1999). The middle temperature peak, a maximum temperature peak at about 250°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

comparison, as the calcination temperature increased, the chlorinated Pt was converted to PtO_2 and the Pt species were strongly interacted with the alumina support due to the higher reduction temperature. However, the part of chlorine present in $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst will be forming oxychlorinated species, which would be more difficult to reduce.

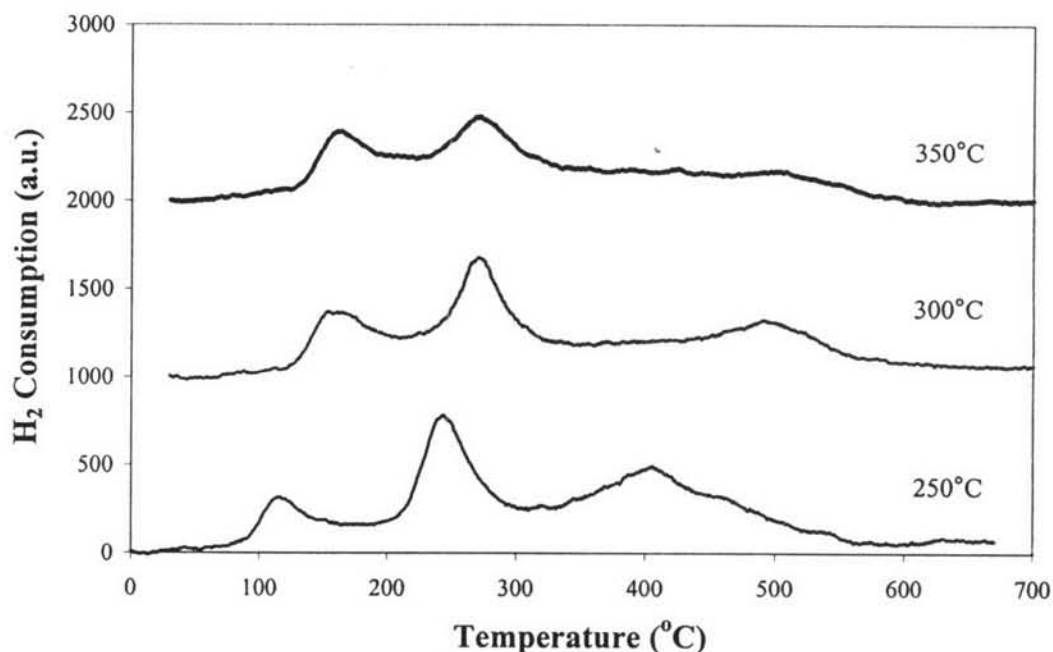


Figure 4.4 TPR profiles of $\text{Pt}/\text{Al}_2\text{O}_3$ with different calcination temperatures.

TPR profiles of F-promoted catalyst prepared with different order of impregnating between Pt and F present different peaks from the Pt without F as shown in Figures 4.5 and 4.6. The TPR profile of $\text{Pt-F}/\text{Al}_2\text{O}_3$ (added F before Pt) had a dominant peak more than $\text{F-Pt}/\text{Al}_2\text{O}_3$ (added Pt before F), may be because F precursor could reduce in the calcination step. Thus, from Figure 4.6 the hydrogen consumption at 170°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 disappearance of hydrogen consumption for $\text{F-Pt}/\text{Al}_2\text{O}_3$ catalysts, especially at high calcination temperature, could be because part of metal had been reduced during calcination of F precursor.

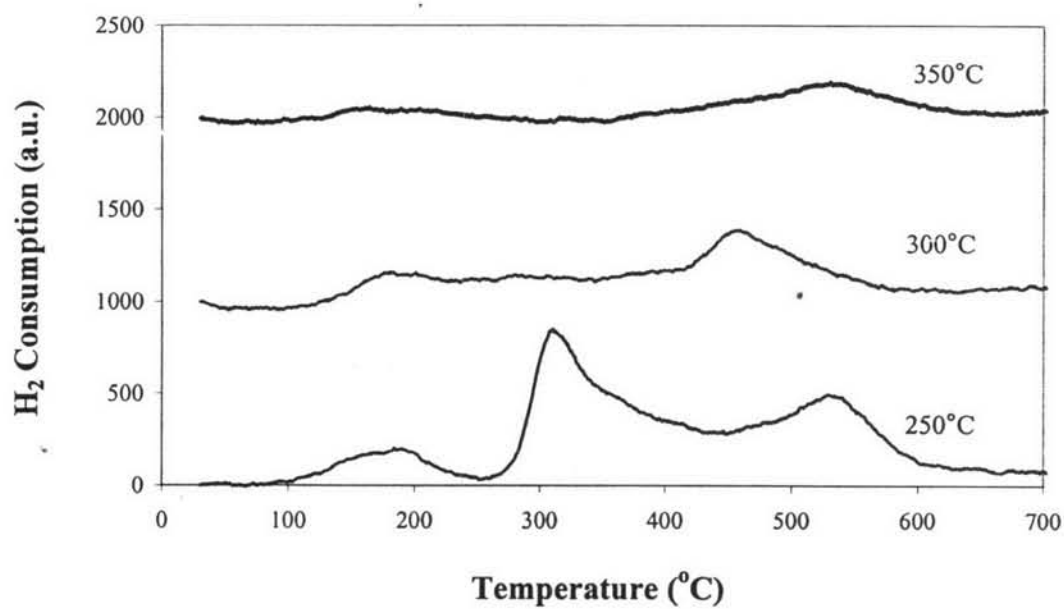


Figure 4.5 TPR profiles of F-Pt/Al₂O₃ with different calcination temperatures.

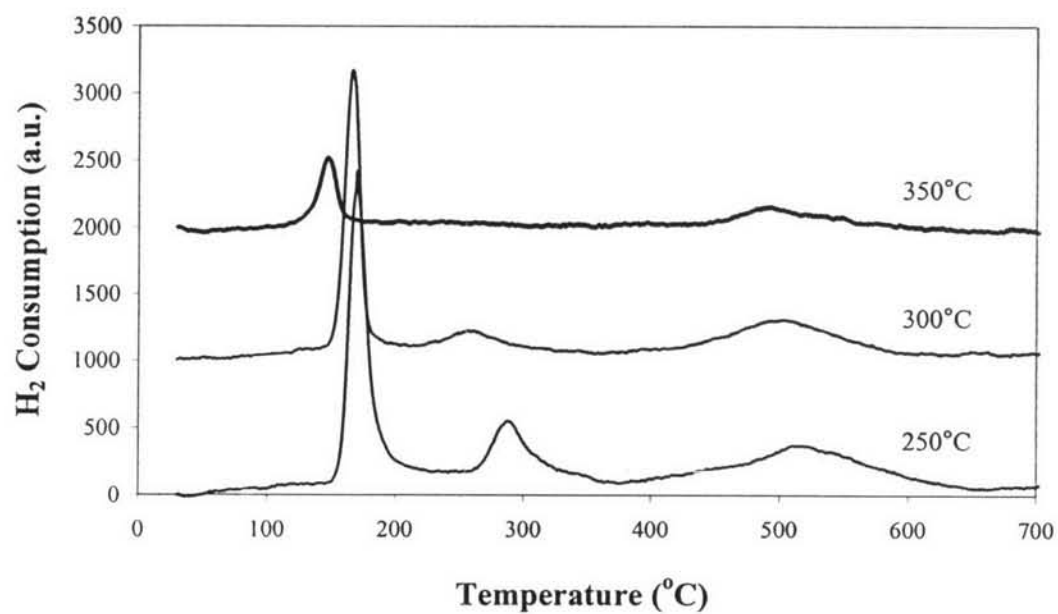


Figure 4.6 TPR profiles of Pt-F/Al₂O₃ with different calcination temperatures.

From Figure 4.7, the TPR profiles of the Pd sample shows a positive peak at 60°C which is the reduction of PdO species and a little negative peak at 100°C, Pd hydride decomposition at 250°C calcination temperature. Desorption of hydrogen from the decomposition of a bulk palladium hydride formed through H-diffusion into the Pd crystallites (Navarro *et al.*, 2000). In addition, the TPR profile of Pd sample shows a broad reduction peak at low calcination temperature. The broadening peak suggested the presence of several Pd species. May be a small amount of chlorine could still present in the calcined Pd/Al₂O₃ catalyst. TPR profile shows high hydrogen consumption for catalyst calcined at low calcination temperature (250°C). It may be concluded that the PdO could still present on the sample. The TPR profile of Pd at 350°C calcination temperature had a peak centered at about 90°C that might correspond to the reduction of particles that have a strong interaction with the support. For the order of impregnation between Pd and F, the F addition at higher calcination temperature dominated hydrogen consumption corresponding to the higher catalytic activity that could be the stronger interaction with the surface as shown in Figures 4.8 and 4.9, respectively. However, the low calcination temperature (250°C) may not be enough to generate metal oxides.

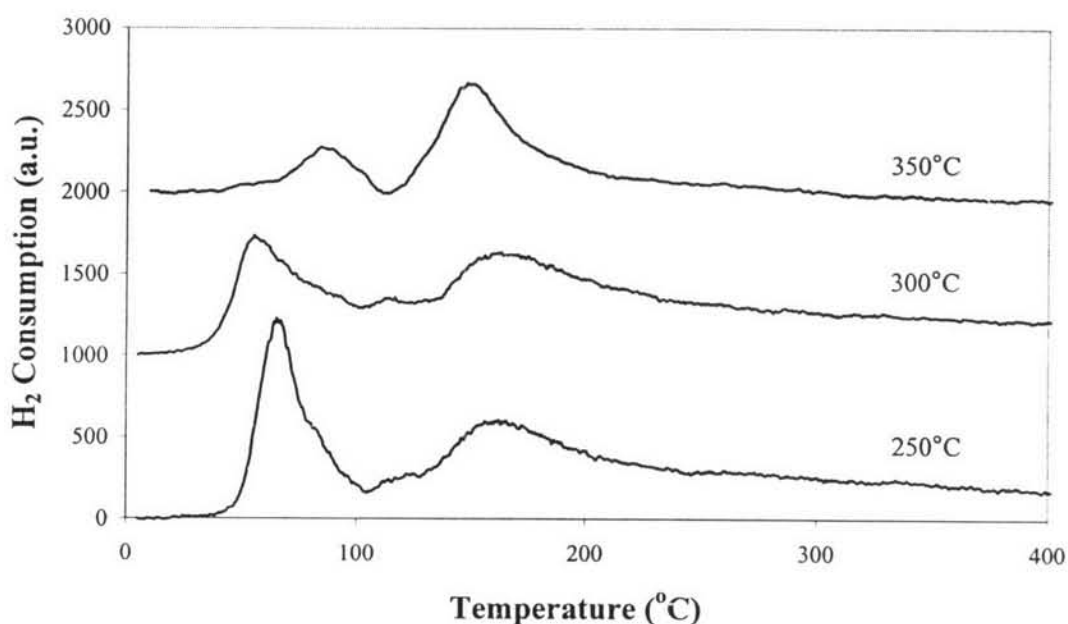


Figure 4.7 TPR profiles of Pd/Al₂O₃ with different calcination temperatures.

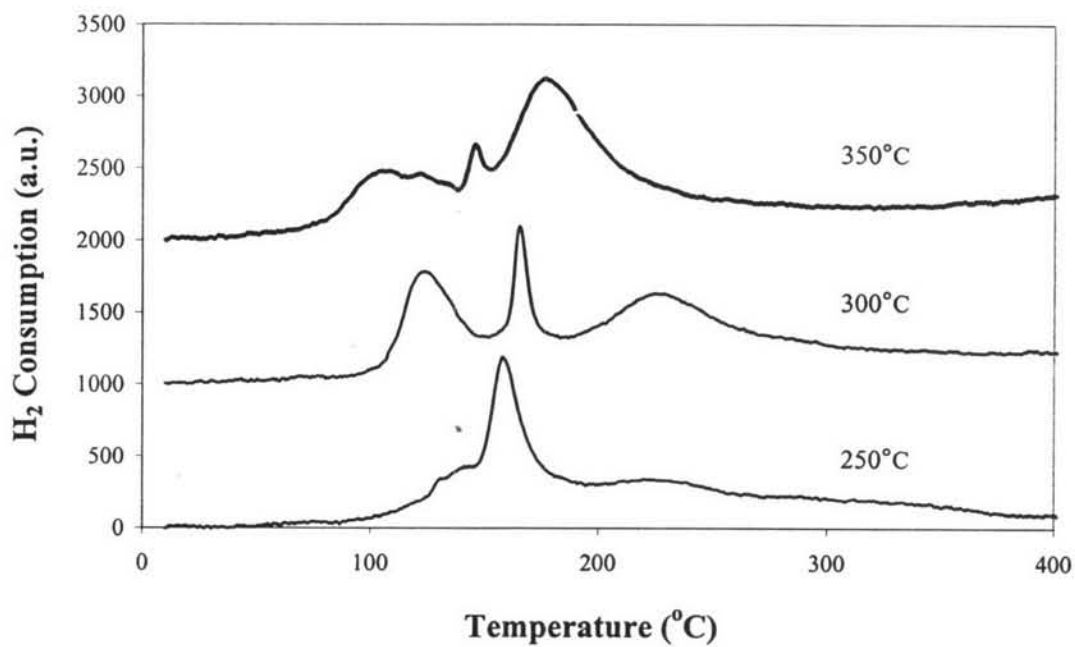


Figure 4.8 TPR profiles of F-Pd/Al₂O₃ with different calcination temperatures.

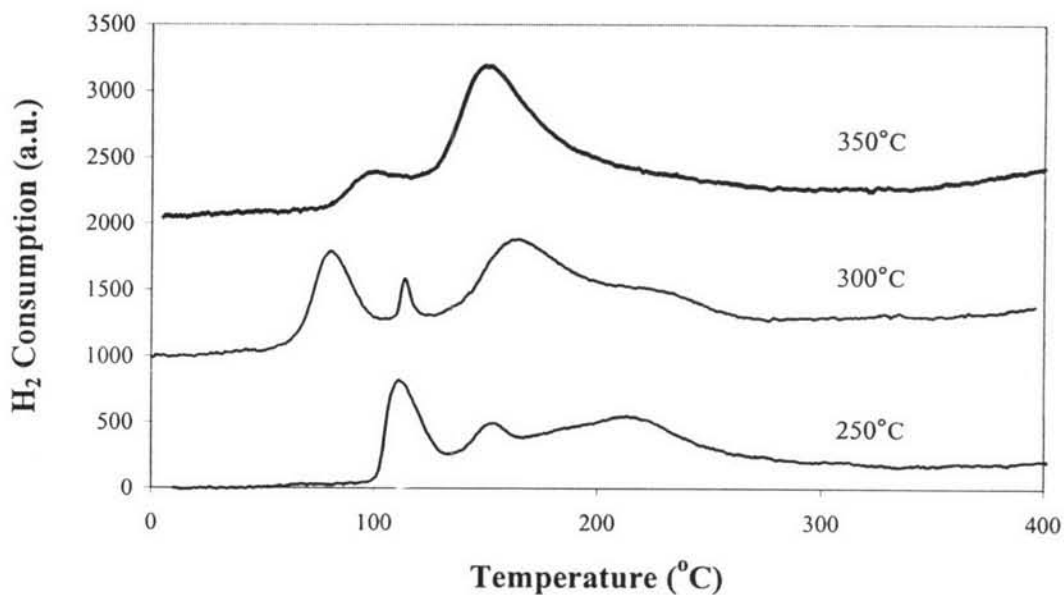


Figure 4.9 TPR profiles of Pd-F/Al₂O₃ with different calcination temperatures.

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 (Figure 4.10) shows an important main reduction zone with a maximum at 80°C in the region that occurs the Pd reduction in the monometallic catalyst. Besides, the broad reduction peak, observed at the region above 150°C where the Pt reduction in the monometallic Pt/Al₂O₃ is produced, indicates a strong interaction between metals, with probable alloys formation at 250°C calcination temperature. However, the interaction between metal and support at high calcination temperature has stronger than at low calcination temperature because of the catalytic action between Pt and Pd during reduction. Comparing with Pt TPR, it may be referred that all Pd oxide was reduced before the reduction of Pt oxide and form the alloy metal. The alloy formation could be catalyzed by the produced Pt⁰, because it may be occurred at higher temperature than on the monometallic Pt. The decrease in hydrogen consumption associated with the PdO species seemed to depend on the presence of Pt. In addition, the second peak around 200°C may indicate the reduction of Pt species together with the co-impregnated Pd, due to some kind of interaction with the surface. The reduction of PtPd without F-promoter seemed to be different from the PtPd with F-promoter. The TPR profiles of PtPd with F-promoter at low calcination temperature may not enough to form alloy formation and the disappearance of peak at 350°C calcination temperature may be inferred that the formation of alloy formation was occurred around 200°C at high calcination temperature. The order of impregnating of PtPd and F-promoter was shown in Figures 4.11 and 4.12, respectively.

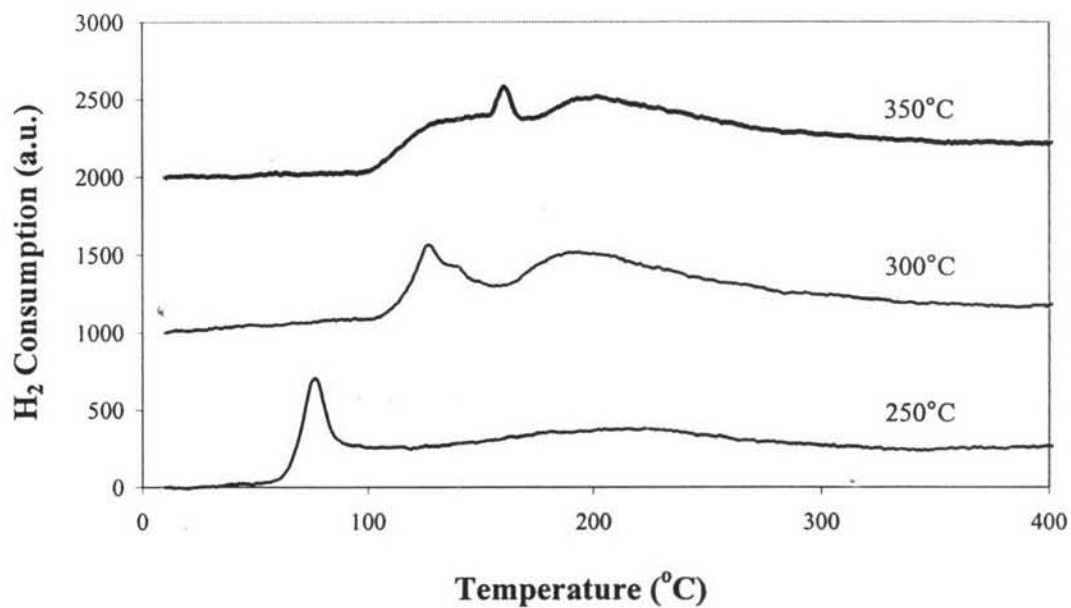


Figure 4.10 TPR profiles of PtPd/Al₂O₃ with different calcination temperatures.

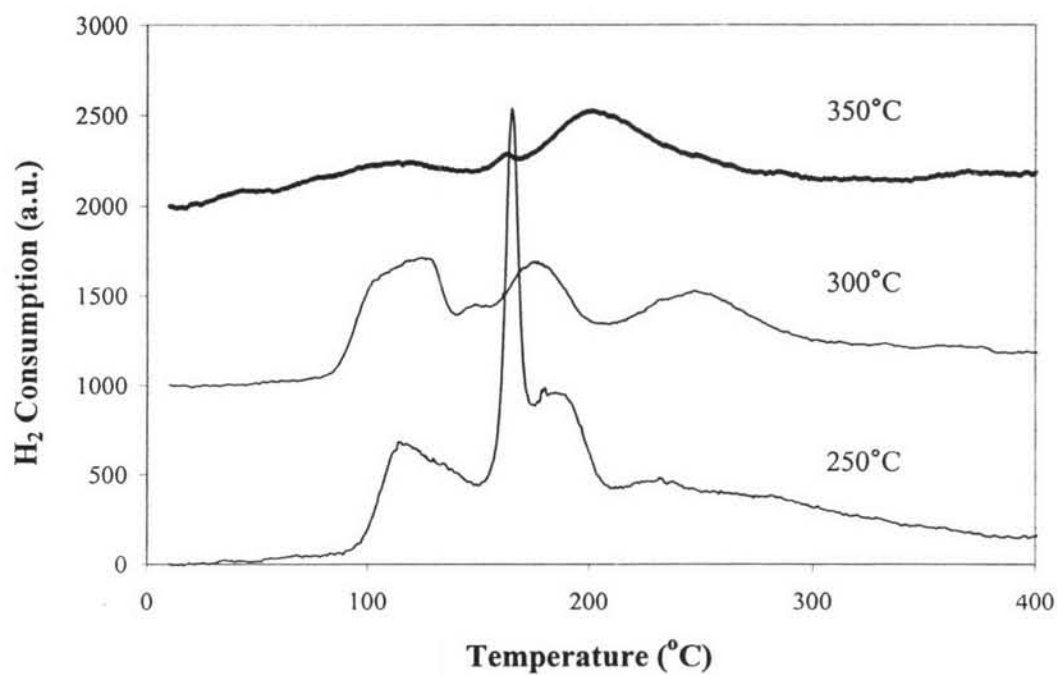


Figure 4.11 TPR profiles of PtPd-F/Al₂O₃ with different calcination temperatures.

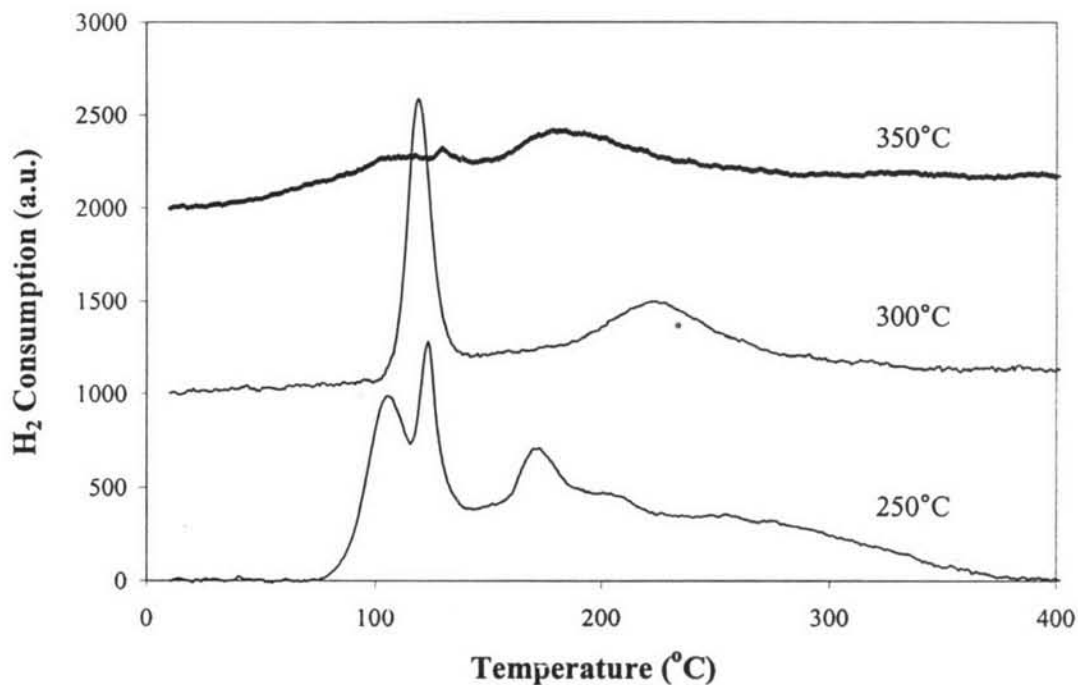


Figure 4.12 TPR profiles of F-PtPd/Al₂O₃ with different calcination temperatures.

However, TPR analysis is not enough to conclude the effect of calcination temperature and the order of impregnation on the catalytic activity. To be explained the effect of calcination temperature and the order of impregnation, other characterization techniques, such as hydrogen chemisorption and Transmission Electron Microscopy (TEM), are also investigated.

4.2.3 Hydrogen Chemisorption

Hydrogen chemisorption is a technique for determining metal dispersion of the catalyst. The dispersion, hydrogen to metal molar ratio (H/metal), 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 in which F was added before metal in both mono- and bi-metallic catalyst but gave the higher metal dispersion in which metal was added before F in both mono- and bi-metallic catalyst, when higher calcination temperature. 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). So, the order of impregnation of metal before F can enhance the metal dispersion which may be the strong interaction in the surface and the higher calcination temperature, the higher metal dispersion.

Table 4.2 List of metal dispersion (H/M) of Pt, Pd, and PtPd with and without F-promoter

Catalyst	Order of impregnation	H ₂ chemisorption (H/M)		
		Calcination temperature (°C)		
		250°C	300°C	350°C
Pt/Al ₂ O ₃	Pt	0.46	0.52	0.54
Pt-F/Al ₂ O ₃	F, Pt	0.33	0.43	0.30
F-Pt/Al ₂ O ₃	Pt, F	0.49	0.58	0.44
Pd/Al ₂ O ₃	Pd	0.32	0.47	0.48
Pd-F/Al ₂ O ₃	F, Pd	0.30	0.32	0.35
F-Pd/Al ₂ O ₃	Pd, F	0.42	0.44	0.61
PtPd/Al ₂ O ₃	PtPd	0.34	0.36	0.41
PtPd-F/Al ₂ O ₃	F, PtPd	0.14	0.14	0.17
F-PtPd/Al ₂ O ₃	PtPd, F	0.18	0.38	0.43

4.2.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscope (TEM) was used to characterize the topology of the catalyst in order to see the metal dispersion on the surface of the catalyst and metal alloy formation. The TEM images of the bi-metallic catalyst with and without F were shown in the Figure 4.13. In TEM image, it is clearly seen the big metal cluster on the surface of γ -alumina of PtPd with F-promoter while PtPd catalyst without F does not see the cluster of metal catalyst which was indicated that the PtPd catalyst has higher metal dispersion than F-PtPd catalyst.

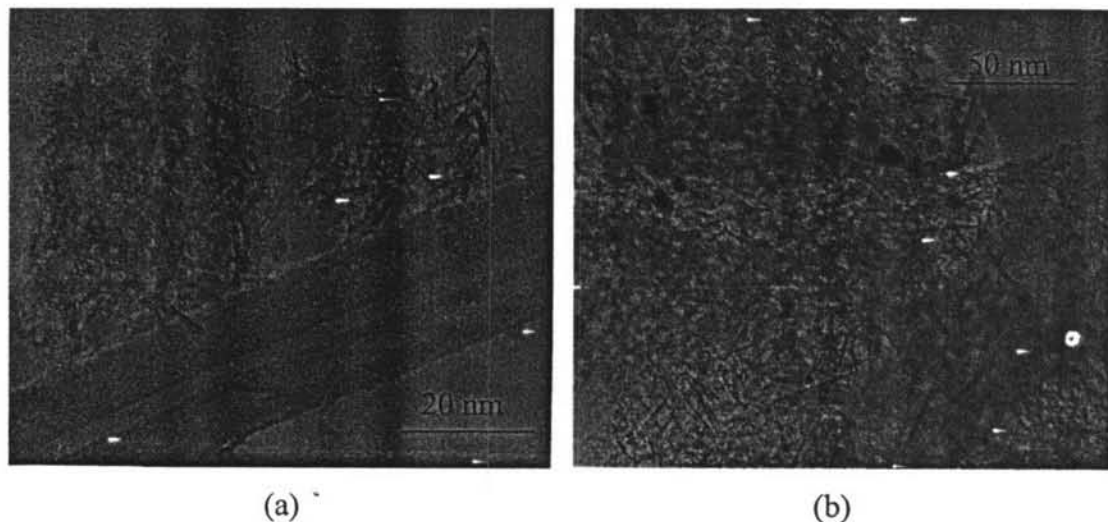
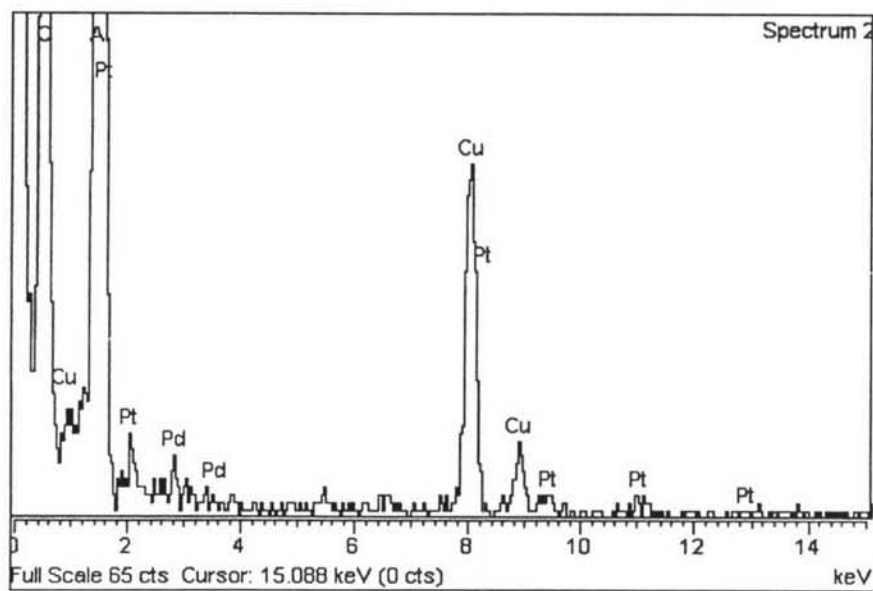
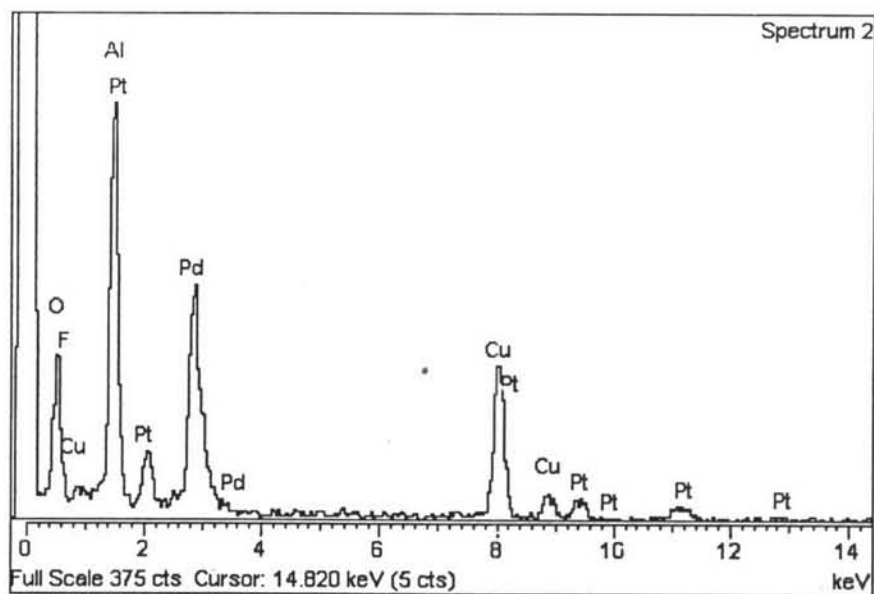


Figure 4.13 TEM images of (a) PtPd/Al₂O₃ (200,000x) and (b) F-PtPd/Al₂O₃ (150,000x) at 250°C calcination temperature.

The TEM-EDX spectra of F-PtPd/Al₂O₃ and PtPd/Al₂O₃ were shown in Figure 4.14 which showed the composition of the catalyst at the selected area diffraction. From the Figure 4.14, Pt, Pd, and F are shown in the spectrum which may be concluded that the alloy formation of bimetallic catalyst could occur.



(a)

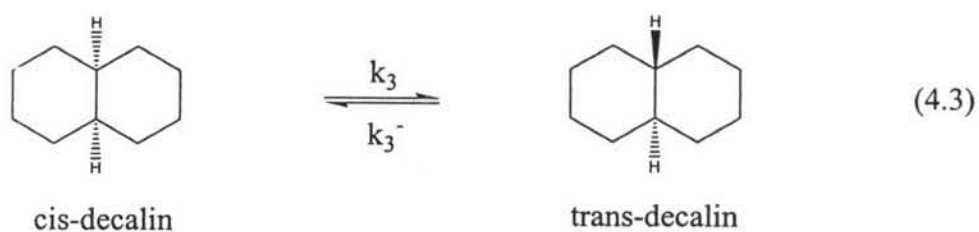
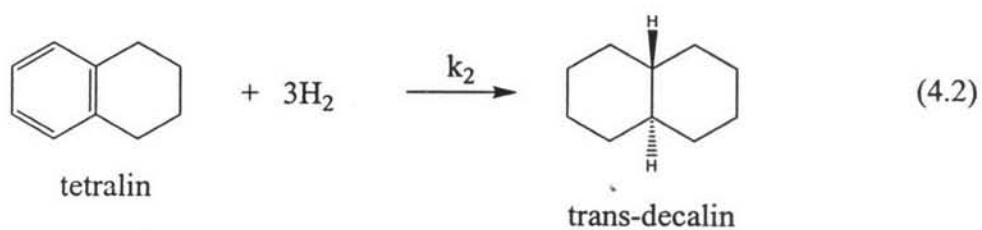
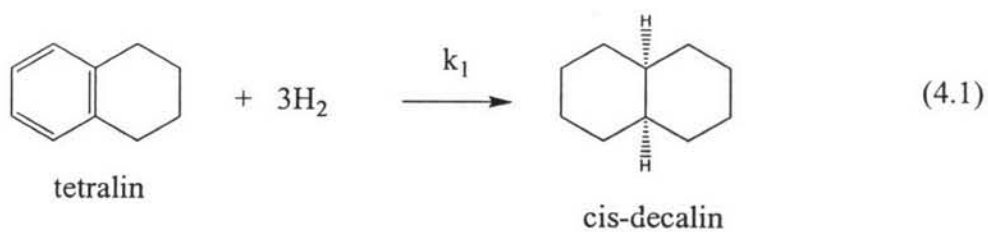


(b)

Figure 4.14 TEM-EDX spectra of (a) PtPd/Al₂O₃ and (b) F-PtPd/Al₂O₃ at 250°C calcination temperature.

4.3 Catalytic Activity

The tetralin hydrogenation was carried out at temperature of 275°C with a constant total pressure of 300 psig and a constant hydrogen/hydrocarbon molar feed ratio of 25. 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:



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).

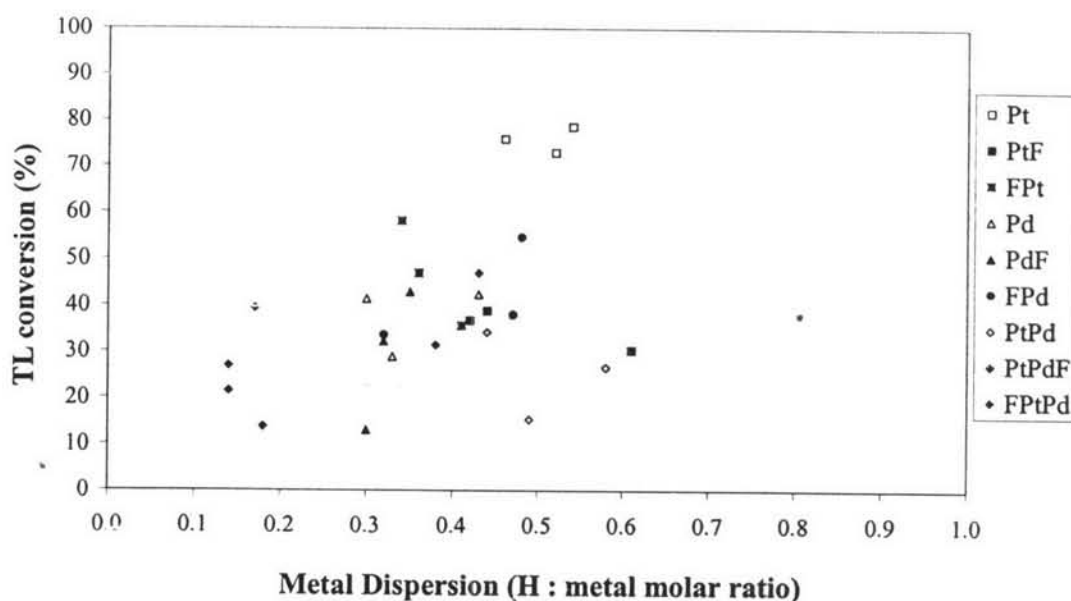


Figure 4.15 The overview of metal dispersion and conversion among catalysts.

Figure 4.15 shows the metal dispersion among catalysts with different calcination temperatures and the order of impregnation depended on the intrinsic properties of the metal. Particularly, Pt metal had very high dispersion and high catalytic activity.

Table 4.3 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. It was seen that Pt had the highest tetralin conversion while Pt with F-promoter had the lower tetralin conversion than Pt without F-promoter corresponding with the metal dispersion of Pt due to F reduced metal dispersion. The order of impregnating between Pt and F-promoter had affected on tetralin conversion, as a result added Pt before F (F-Pt/ Al_2O_3) can enhance the tetralin conversion more than added F before Pt (Pt-F/ Al_2O_3). Since F can replace the hydroxyl group of alumina which reduces the surface area of metal (Ghosh and Kydd, 1985). On the other hand, the conversion of Pd and PtPd/ Al_2O_3 was lower than Pt due to the intrinsic properties of Pd. The conversion of PtPd/ Al_2O_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 4.3 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	250	75.91	0.46
Pt/Al ₂ O ₃	300	73.00	0.52
Pt/Al ₂ O ₃	350	78.64	0.54
Pt-F/Al ₂ O ₃	250	36.75	0.33
Pt-F/Al ₂ O ₃	300	38.82	0.43
Pt-F/Al ₂ O ₃	350	30.38	0.30
F-Pt/Al ₂ O ₃	250	58.23	0.49
F-Pt/Al ₂ O ₃	300	46.98	0.58
F-Pt/Al ₂ O ₃	350	35.68	0.44
Pd/Al ₂ O ₃	250	28.93	0.32
Pd/Al ₂ O ₃	300	42.42	0.47
Pd/Al ₂ O ₃	350	45.77	0.48
Pd-F/Al ₂ O ₃	250	13.00	0.30
Pd-F/Al ₂ O ₃	300	32.19	0.32
Pd-F/Al ₂ O ₃	350	51.04	0.35
F-Pd/Al ₂ O ₃	250	33.63	0.42
F-Pd/Al ₂ O ₃	300	38.06	0.44
F-Pd/Al ₂ O ₃	350	54.72	0.61
Pt-Pd/Al ₂ O ₃	250	15.36	0.34
Pt-Pd/Al ₂ O ₃	300	26.64	0.36
Pt-Pd/Al ₂ O ₃	350	34.21	0.41
PtPd-F/Al ₂ O ₃	250	21.47	0.14
PtPd-F/Al ₂ O ₃	300	26.95	0.14
PtPd-F/Al ₂ O ₃	350	39.42	0.17
F-PtPd/Al ₂ O ₃	250	13.70	0.18
F-PtPd/Al ₂ O ₃	300	31.48	0.38
F-PtPd/Al ₂ O ₃	350	46.96	0.43

From Figure 4.16, the difference in calcination temperatures for Pt/Al₂O₃ does not result in significant difference in conversion but it does for Pd/Al₂O₃ and PtPd/Al₂O₃ as shown in Figures 4.17 and 4.18, respectively. It may be due to the strong interaction with the surface of Pt.

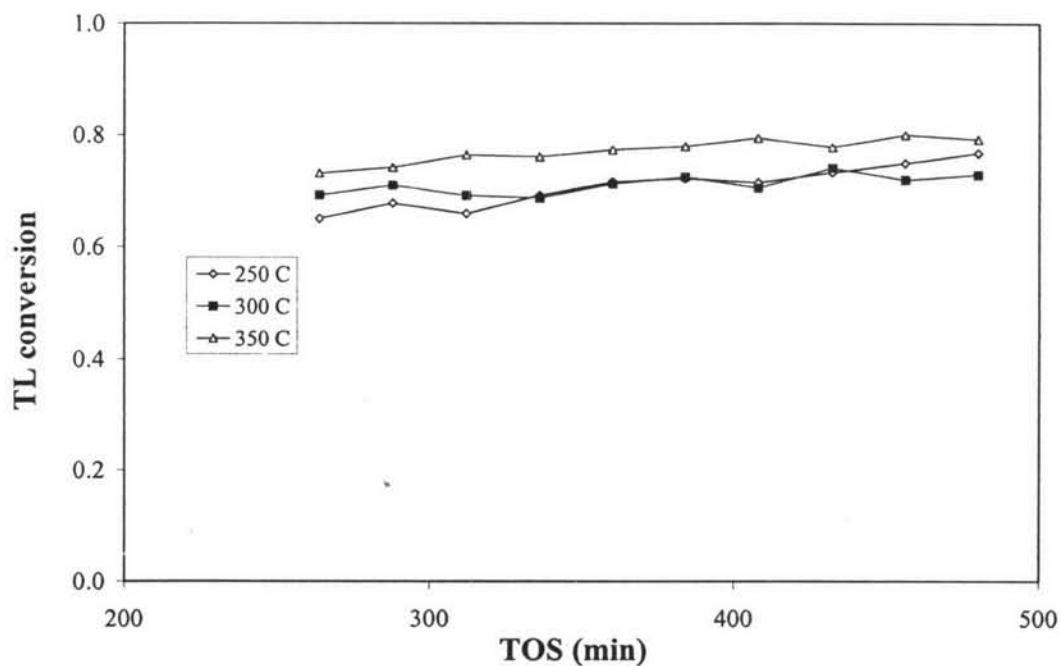


Figure 4.16 Conversion of tetralin as a function of time on stream (TOS) over Pt/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.

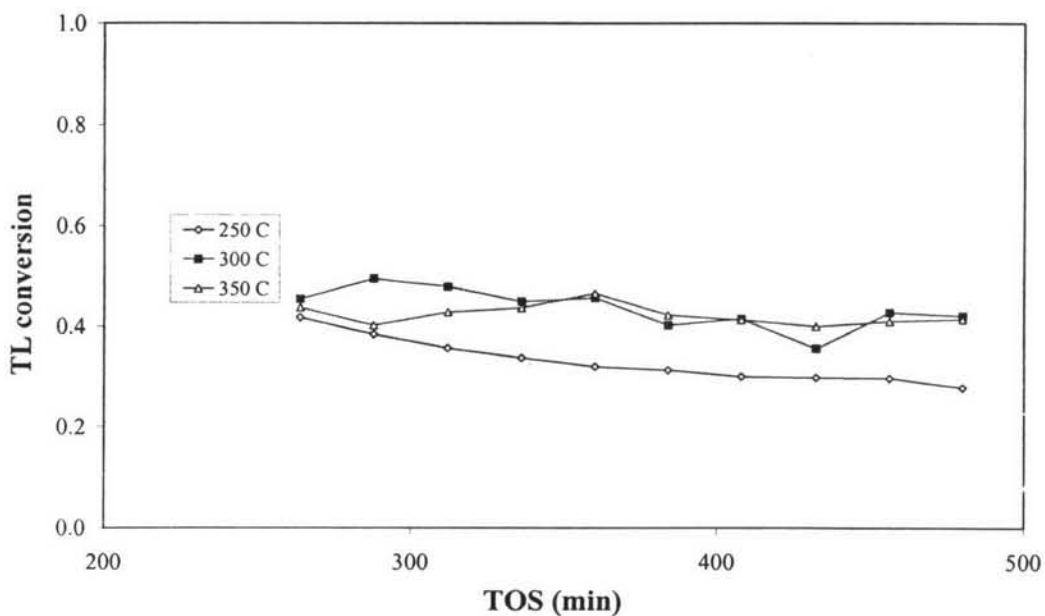


Figure 4.17 Conversion of tetralin as a function of time on stream (TOS) over Pd/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.

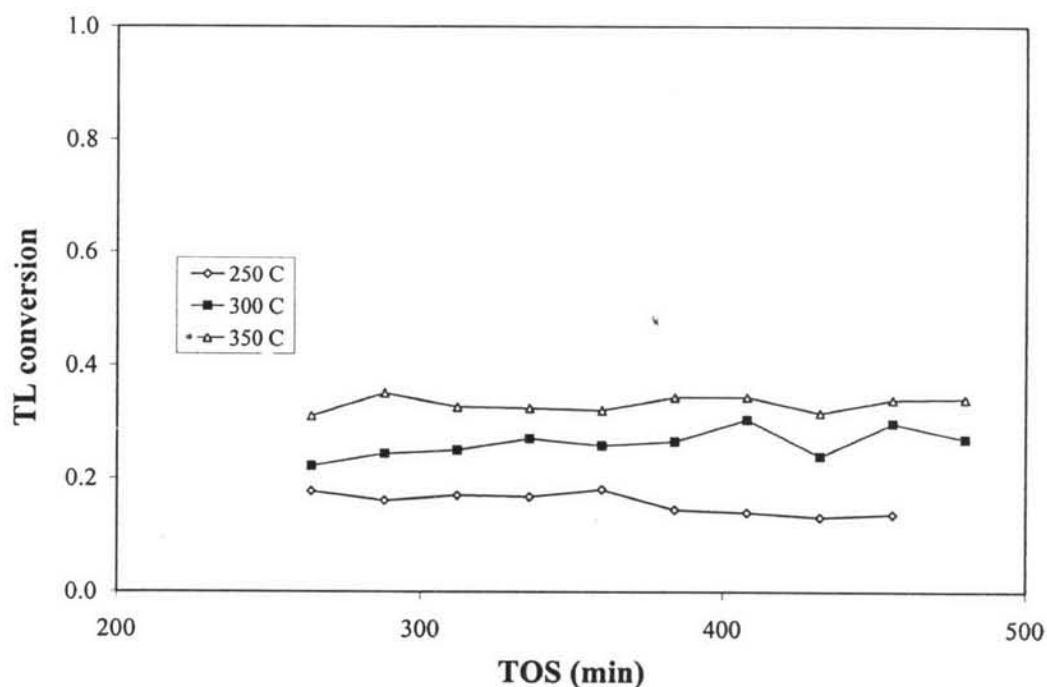


Figure 4.18 Conversion of tetralin as a function of time on stream (TOS) over PtPd/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.

The fluorine addition showed clearly different tetralin conversion on Pt, Pd and PtPd/Al₂O₃ at different calcination temperatures as shown in Figures 4.19, 4.20, 4.21, 4.22, 4.23, and 4.24, respectively. The presence of F on Pd caused an increase in the catalytic activity due to the strong interaction of catalyst. The F-Pt/Al₂O₃ catalyst prepared with calcination temperature at 250°C had a higher tetralin conversion than other calcination temperatures that could be due to the agglomeration of Pt which is easily happened at higher calcination temperature. Moreover, 300°C calcination temperature was suitable for Pt/Al₂O₃ with F-promoter due to the agglomeration during calcination in the presence of F-precursor at higher calcination temperature while 350°C calcination temperature for Pd/Al₂O₃ and PtPd/Al₂O₃ with and without F-promoter had the highest tetralin conversion because of the isomerization of Pd and the trend of PtPd-F/Al₂O₃ and F-PtPd/Al₂O₃ was similar to Pd-F/Al₂O₃ and F-Pd/Al₂O₃, respectively.

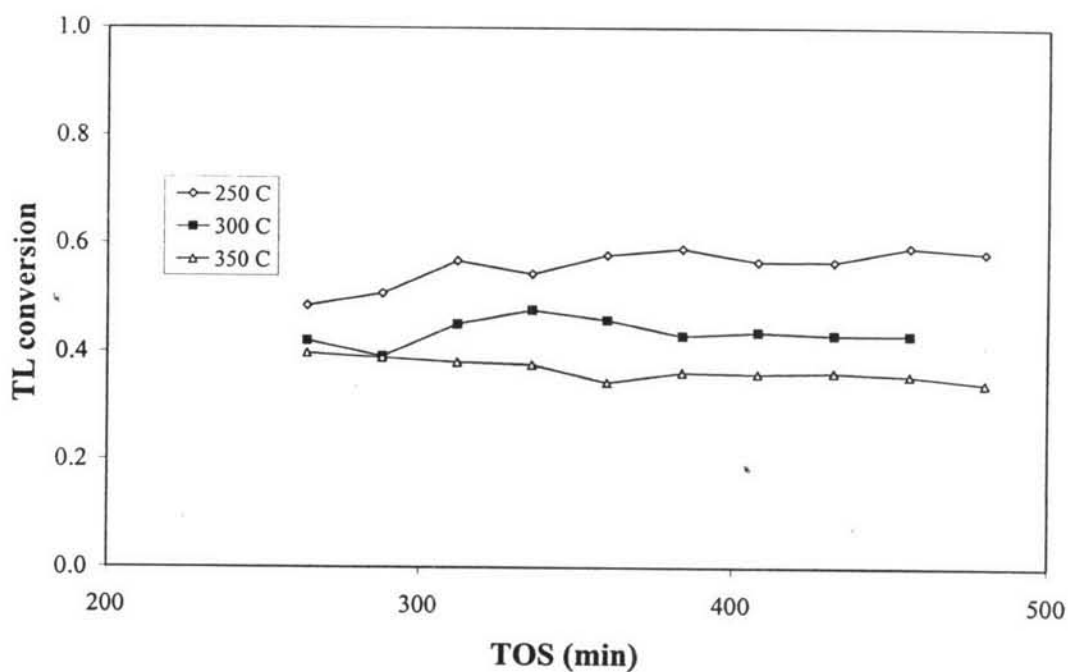


Figure 4.19 Conversion of tetralin as a function of time on stream (TOS) over F-Pt/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.

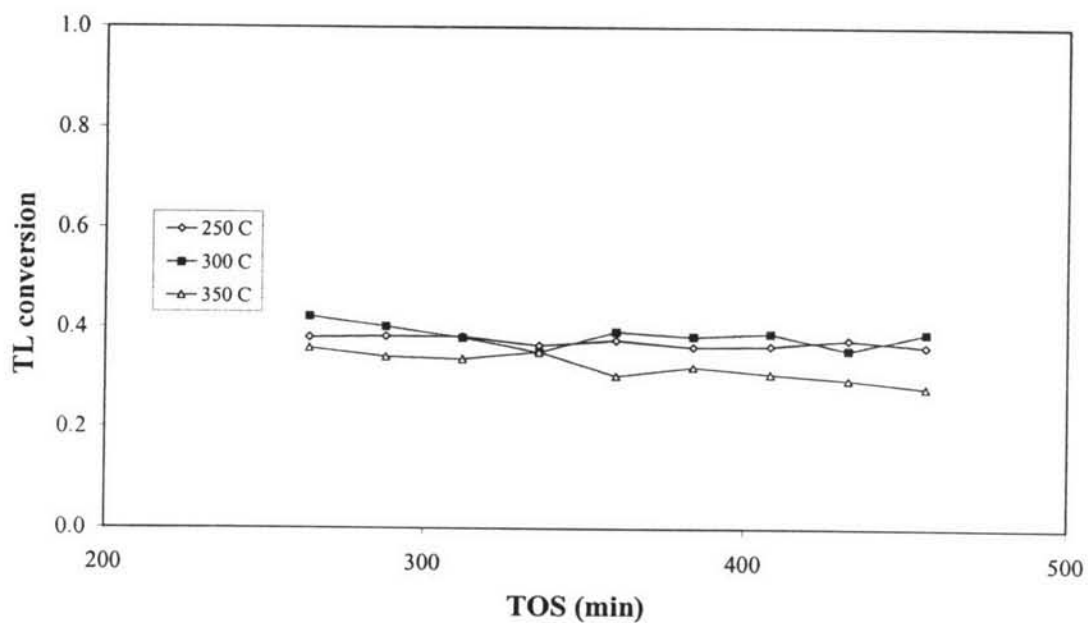


Figure 4.20 Conversion of tetralin as a function of time on stream (TOS) over Pt-F/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.

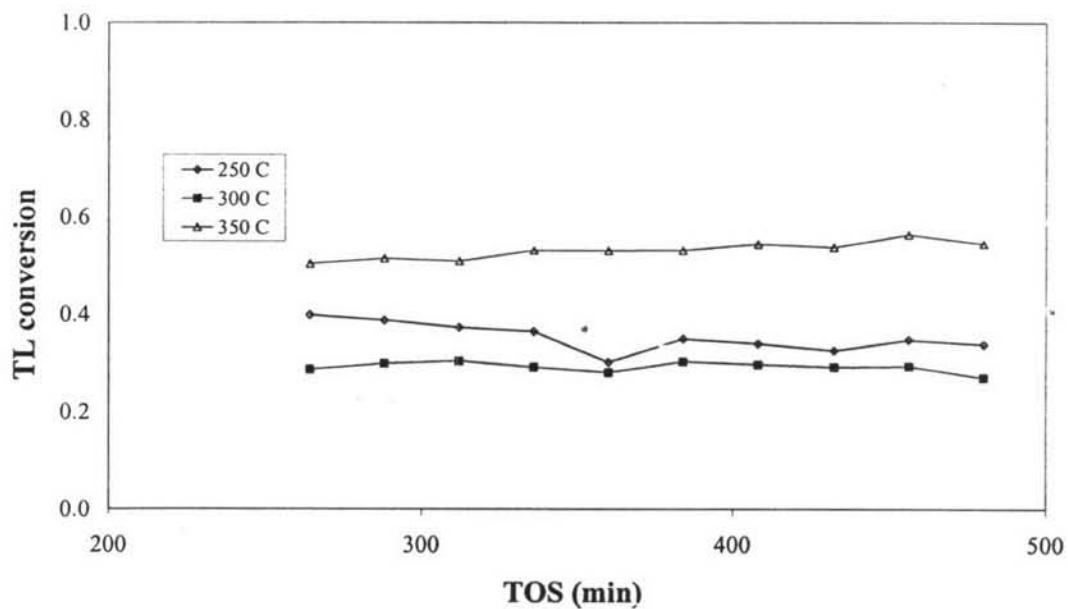


Figure 4.21 Conversion of tetralin as a function of time on stream (TOS) over F-Pd/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.

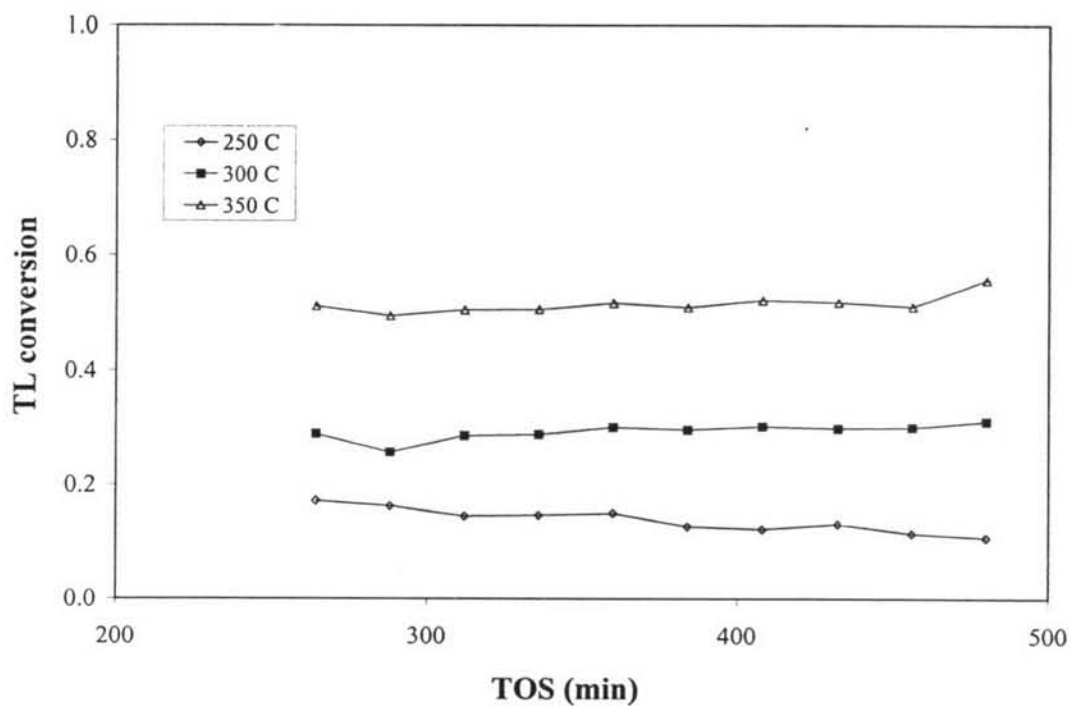


Figure 4.22 Conversion of tetralin as a function of time on stream (TOS) over Pd-F/Al₂O₃. Reaction condition: 300 psig, H₂/HC=25.

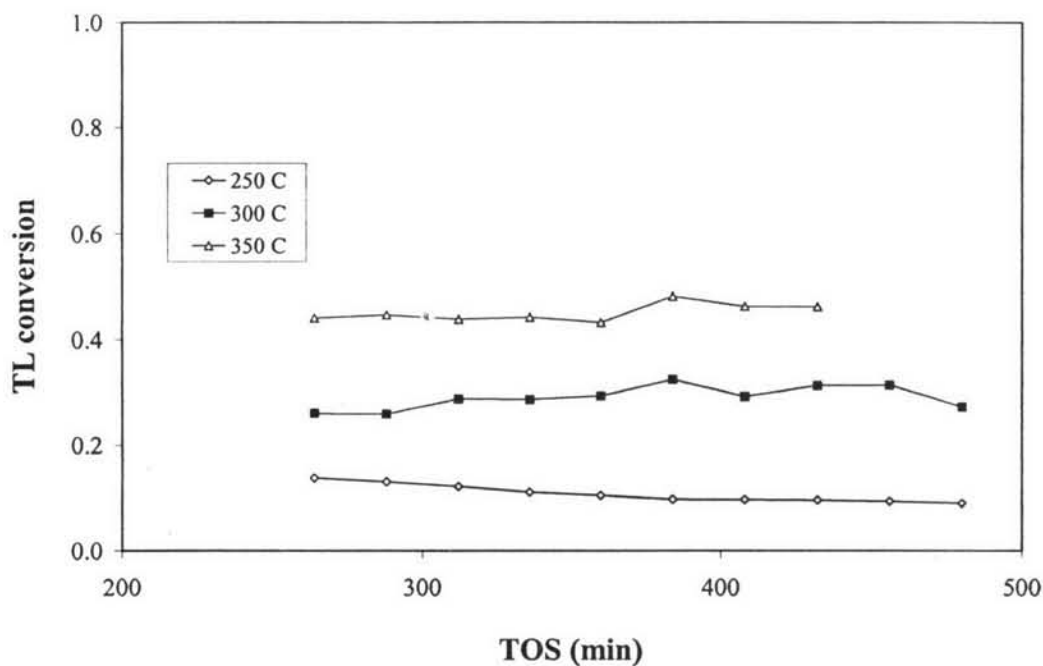


Figure 4.23 Conversion of tetralin as a function of time on stream (TOS) over F-PtPd/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.

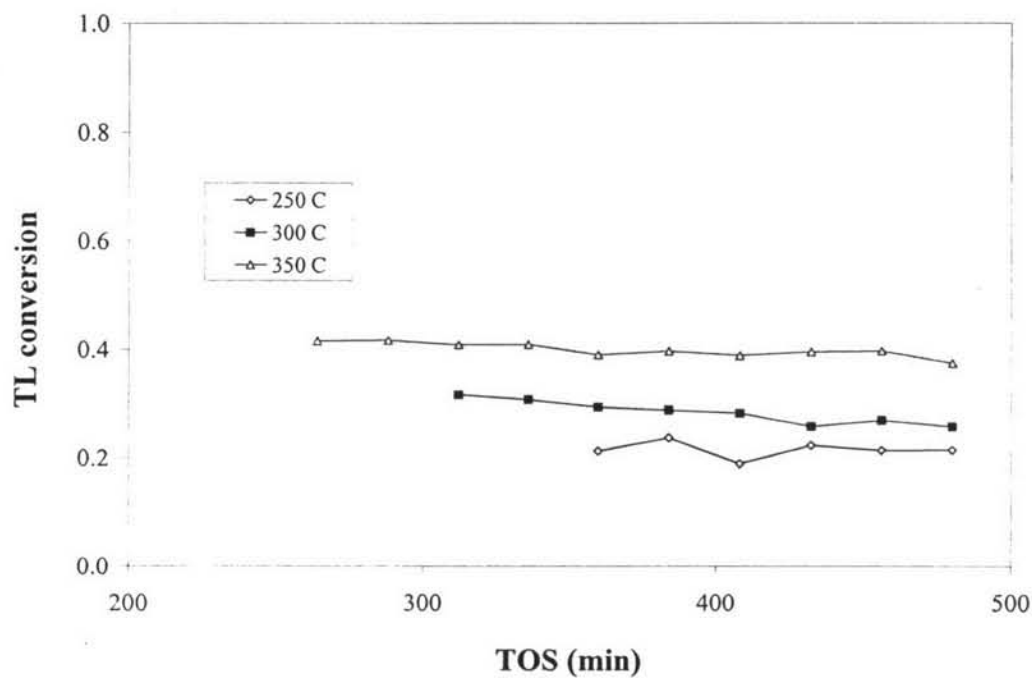


Figure 4.24 Conversion of tetralin as a function of time on stream (TOS) over PtPd-F/Al₂O₃. Reaction condition: 300 psig, 275°C, H₂/HC=25.