CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst characterization

From TEM images, metal particle sizes of 7 - 10 nm in diameter were observed as shown in Figure 4.1. This corresponds to about 7% dispersion which is rather low for a typical catalyst. The oxygen-nitrogen titration experiment was conducted with the attempt to obtain the dispersion and then compare with that obtained from TEM. However, due to the very low Pd loading, the amount of hydrogen uptake observed was so low that the difference between the highest uptake and the lowest uptake (41.47 %) was within the experimental error (56.83 %). The error in the detecting of unadsorbed and unabsorbed hydrogen was obtained from observing the amount of this hydrogen detected by the chemisorption instrument for several injections of hydrogen without catalyst. The error may be the result of inconsistency in the amount of hydrogen injected or the leakage in the instrument. In addition, since the catalyst contains silver which can both adsorb and absorb oxygen, this may lead to a rather complex sorption mechanism in which a simple oxygen - hydrogen titration cannot be applied to determine the active site and dispersion of the catalyst.

The TPD experiment was performed over the temperature range of 40-700 ° C. The Pd-Ag/ Al_2O_3 catalyst was first reduced in pure, flowing hydrogen for 2 hours at 200 °C and then was exposed to 55 ml/min of hydrogen for 15 mins at room temperature. TPD experiments were conducted by heating

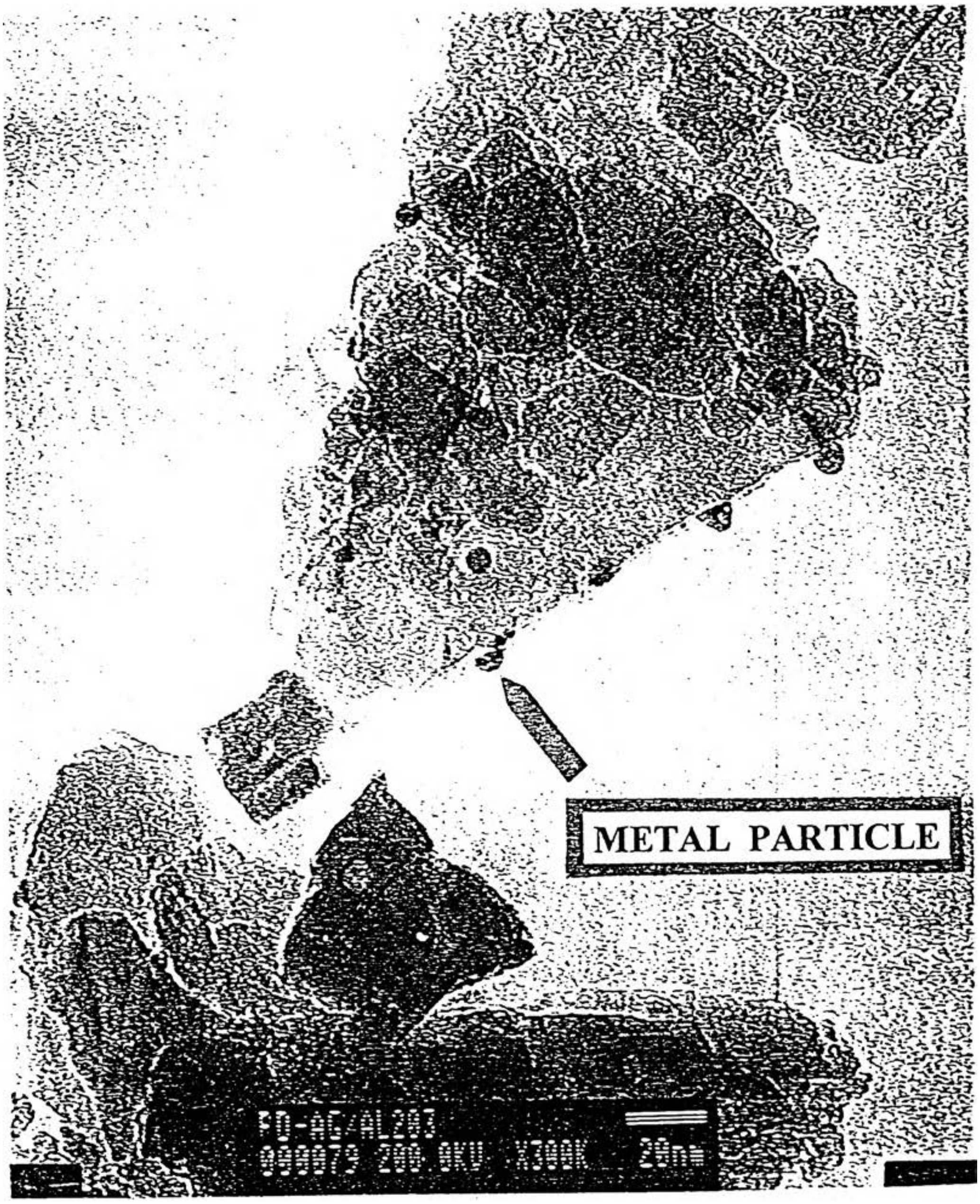

Figure 4.1 Transmission electron microscopy (TEM) image.

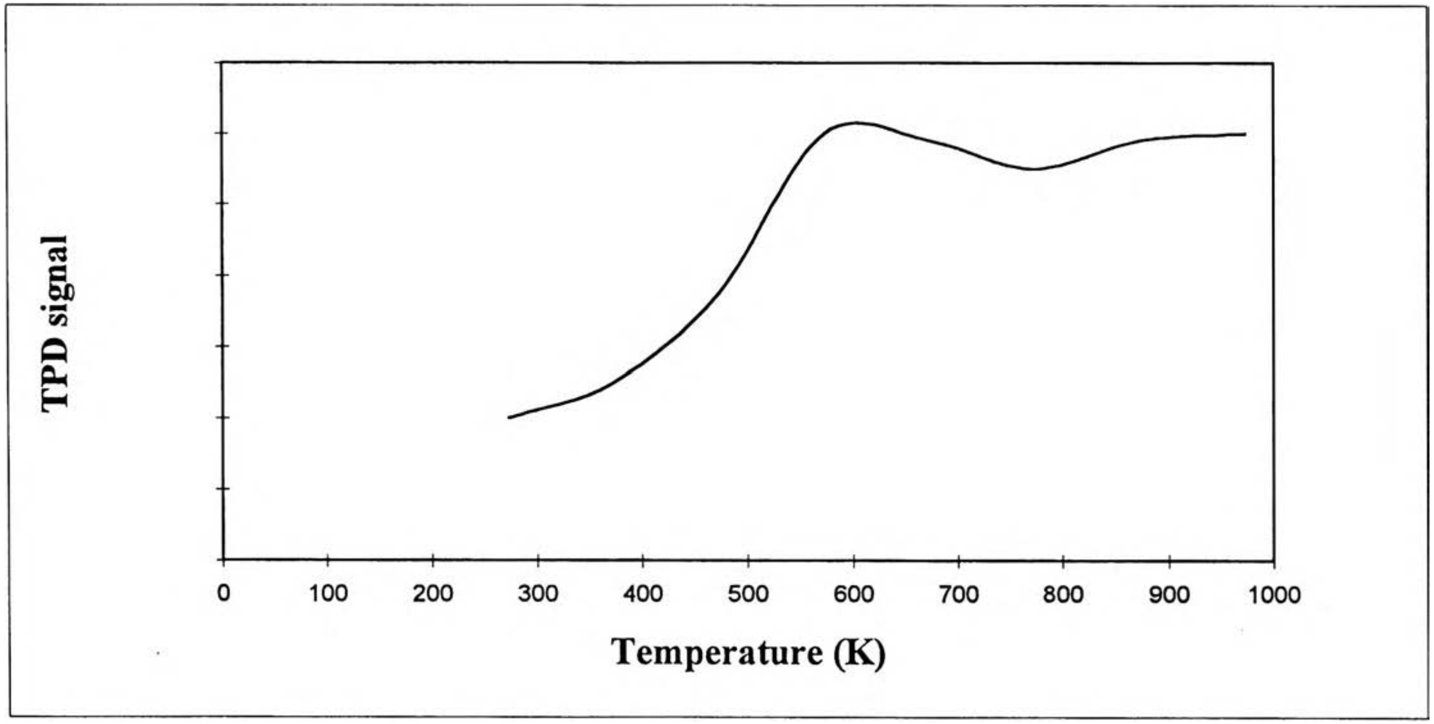

Figure 4.2 The temperature program desorption curve.

the sample in a stream of pure nitrogen at a heating rate of 5 °C/sec. The obtained spectra (Figure 4.2) shows two broad peaks. The first peak starts at 40 ° C and ends at the temperature around 490 ° C. At higher temperature, a second broad peak starts to develop, and even at 700 °C, hydrogen still comes off the sample. This suggests that under the experimental conditions, some of the hydrogen may not completely desorb from the palladium even at 700 °C.

4.2 Kinetics studies

4.2.1 External limitation

For both ethylene hydrogenation and acetylene hydrogenation, it can be seen from Fig 4.3 and Fig. 4.4 that the curves leveled off at appoximately 200 ml/min of the total feed stream. The region of flow rate that has no external limitation starts at 200 ml/min. In this work, according to the lower limit in flow rate range of mass flow controller used, the total flow rate of 300 ml/min was used for all of the experiments.

4.2.2 Kinetics studies of ethylene hydrogenation

From Figures 4.5, 4.6 and 4.7, the gradual decrease in slope of the deactivation curves in the ethylene hydrogenation may be the result of the gradual build-up of the carbonaceous deposits which consist mainly of C_{4+} oligomers acting as catalyst fouling agents. The spent catalyst did not change much in color. The change can only be noticed by placing the fresh catalyst and the spent catalyst next to each other and compare them. This implied that there is only a small amount of carbonaceous deposit on the catalyst.

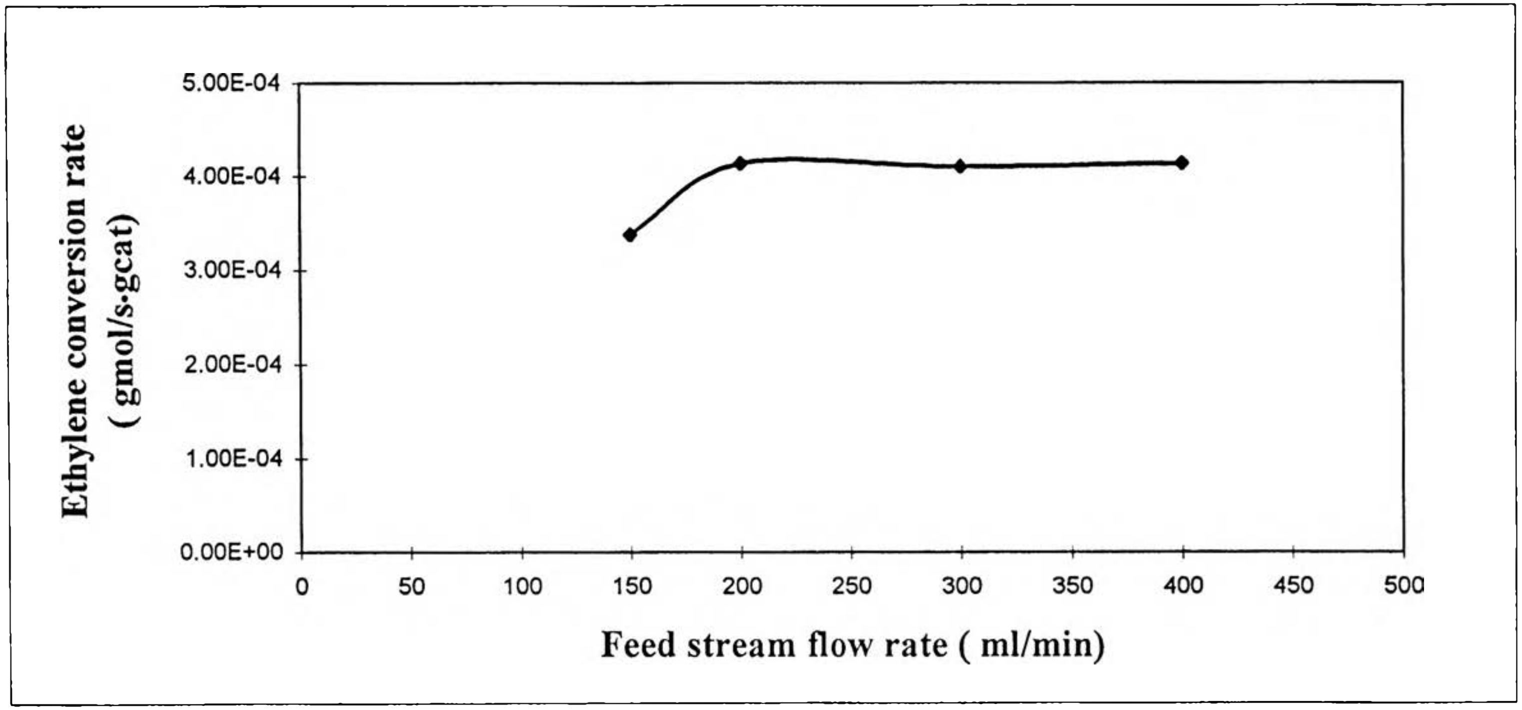

Figure 4.3 The test of external limitation for ethylene hydrogenation experiment at 3 mol% hydrogen 30 mol% ethylene and 80 °C.

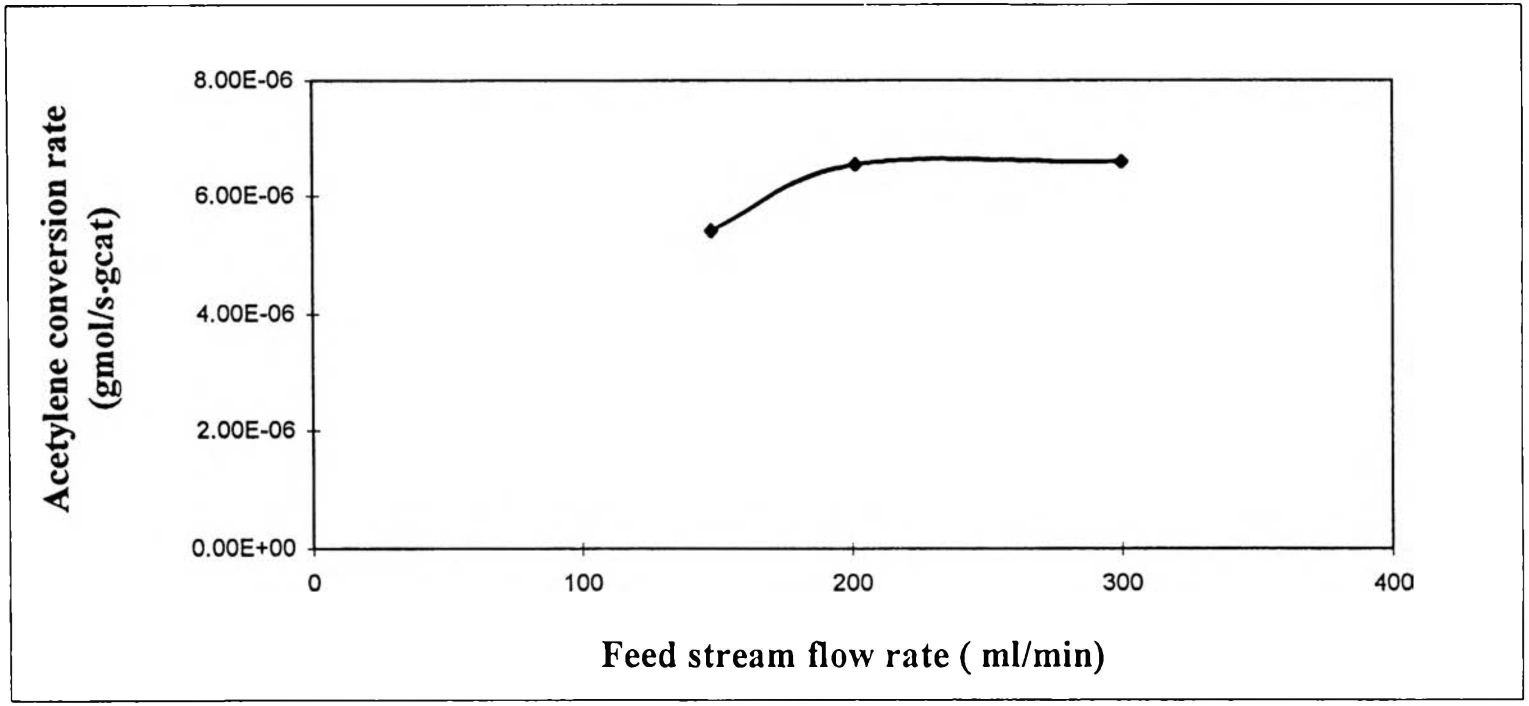

Figure 4.4 The test of external limitation for acetylene hydrogenation experiments at 2 mol% hydrogen 1 mol% acetylene and 80 °C.

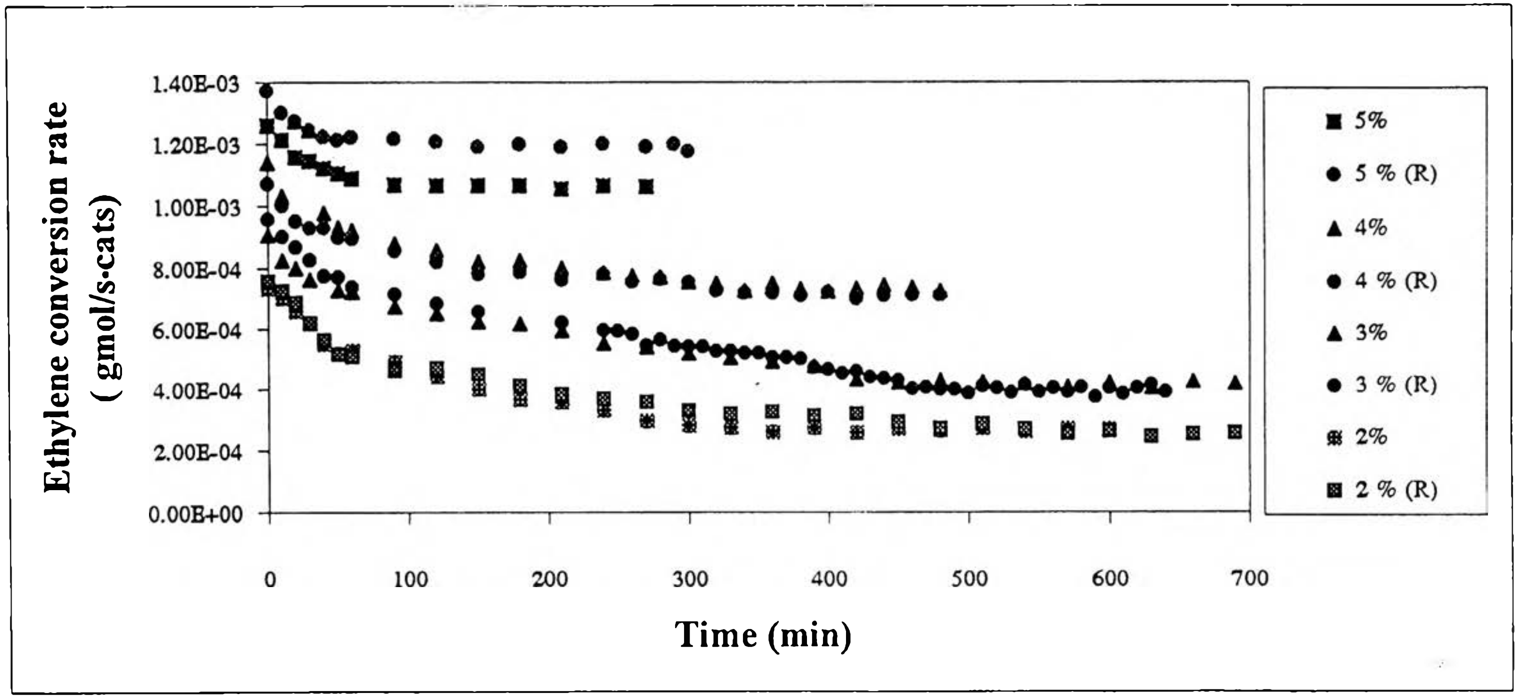

Figure 4.5 Deactivation curve for hydrogen dependence of ethylene hydrogenation experiments at 30 mol% ethyelen and 80 °C.

Note : Hydrogen concentration were shown in the legend. R denotes the repeating experiment.

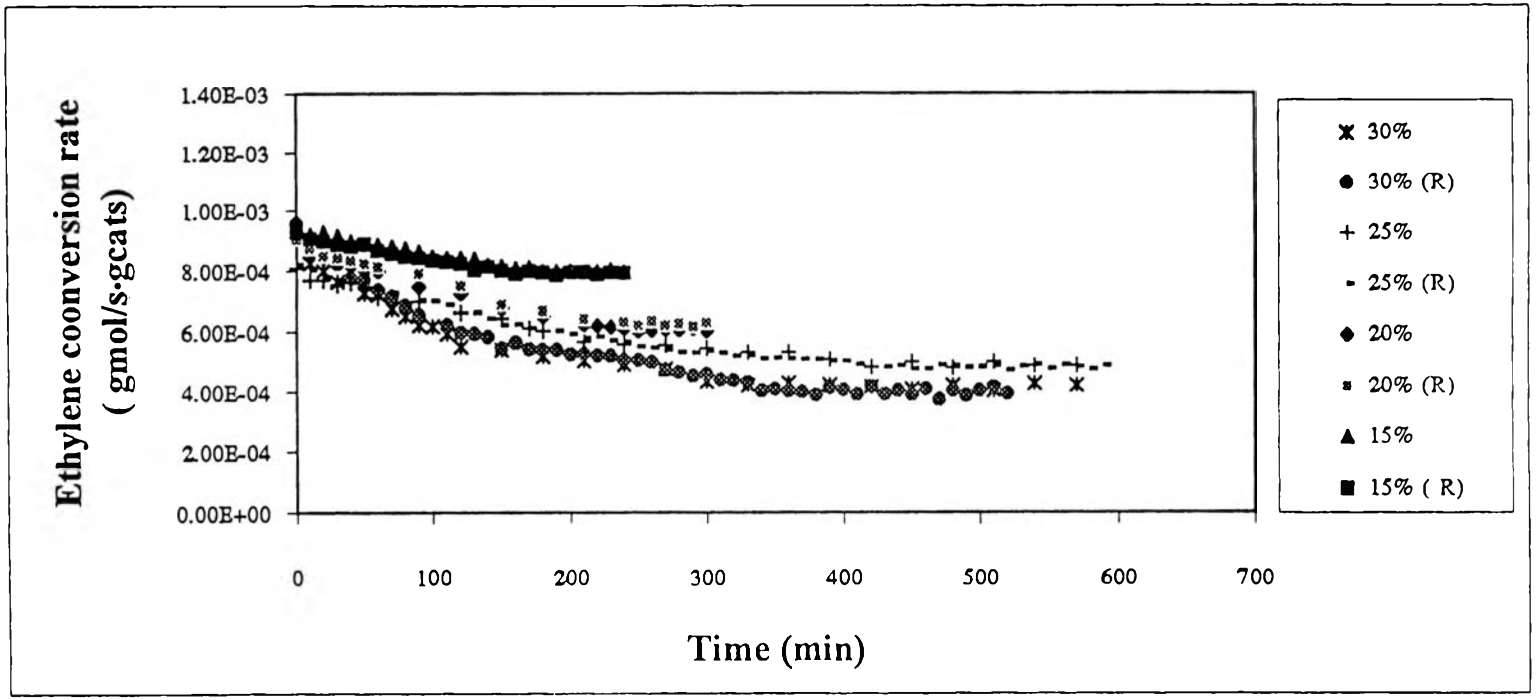

Figure 4.6 Deactivation curve for ethylene dependence of ethylene hydrogenation at 3 mol% hydrogen and 80 °C.

Note : Ethylene concentration were shown in the legend. R denotes the repeating experiment.

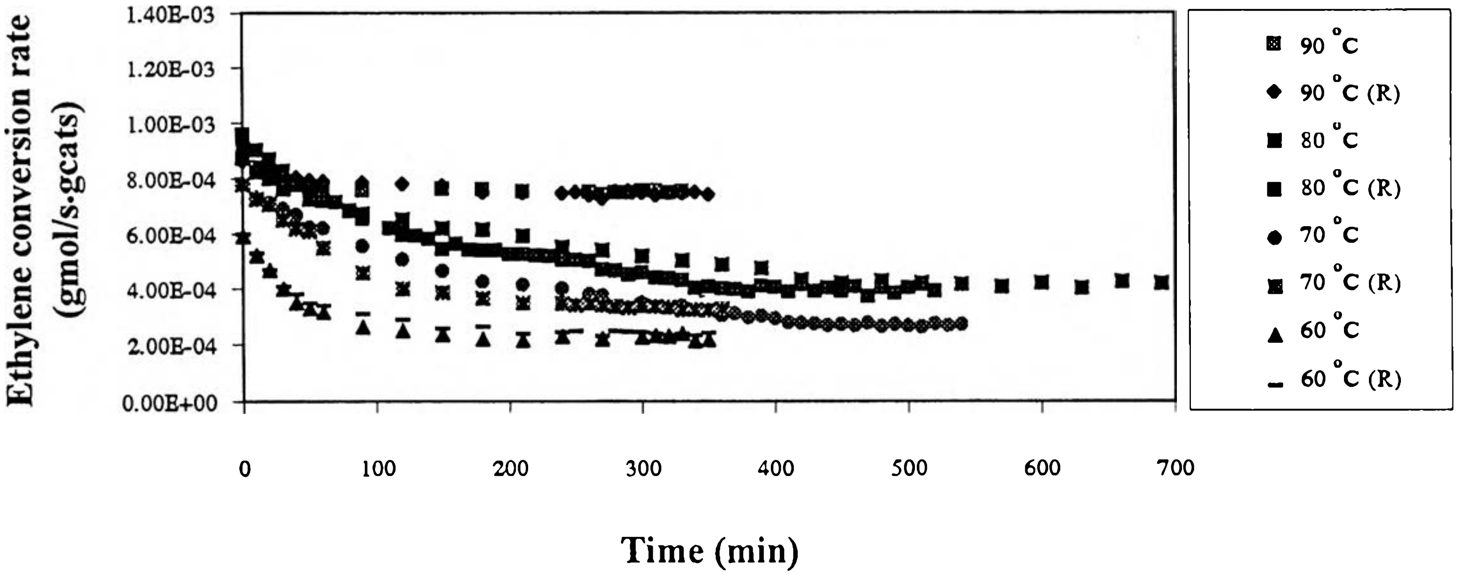

Figure 4.7 Deactivation curve for temperature dependence of ethylene hydrogenation at 3 mol % hydrogen and 30 mol % ethyelene.

Note : Reaction temperature were shown in the legend. R denotes the repeating experiment.

Fig. 4.5 shows the effect of hydrogen concentration on deactivation rates. The adsorption of hydrogen on the Pd surface may decrease the possibility of ethylene adsorption resulting in decreased formation of carbonaceous deposits and thus, better activity maintenance. At 5 % hydrogen, the catalyst loses only about 15 % activity (Table 4.1) within the first hour on stream, and then lines out into a steady state activity. In contrast, at 4 %, 3 %, and 2 % hydrogen, the catalyst loses about 35 %, 56 %, and 64 % of its initial activity, respectively, with a steep decline in the first hour followed by further gradual decrease in activity until steady state operations are reached. Figure 4.8 summarizes the effect of hydrogen concentration on the relative degree of deactivation at 80 °C and with 30% ethylene concentration. There is a nearly linear decrease of relative deactivation with increasing hydrogen concentration.

The carbonaceous deposits are proposed to be the product of dissociatively adsorbed ethylene which is favored by the high ethylene concentration. As a result, operating at higher ethylene concentration should lead to increased formation of carbonaceous deposits and, consequently, cause more severe catalyst deactivation at faster deactivation rates. The experimental results (Fig. 4.6) confirm this and show a linear trend between increasing ethylene concentration and degree of deactivation (Figure 4.9). At higher concentration of ethylene, the initial rates of deactivation are higher, but due to the more severe degree of deactivation it takes longer to reach a final steady state activity. Apart from the ethylene concentration, one would expect the formation of the deposits to be favored by an increase in reaction temperature. At higher temperatures, the degree of deactivation and the deactivation rates should go up. From Fig. 4.7, one can see that the results do not agree with this hypothesis. In fact, at the lowest temperature, 60 °C, the initial rate of deactivation was the highest, and the relative degree of deactivation was about 62 %. Similar results, 62 % deactivation, were observed at 70 °C, and at 80 °C,

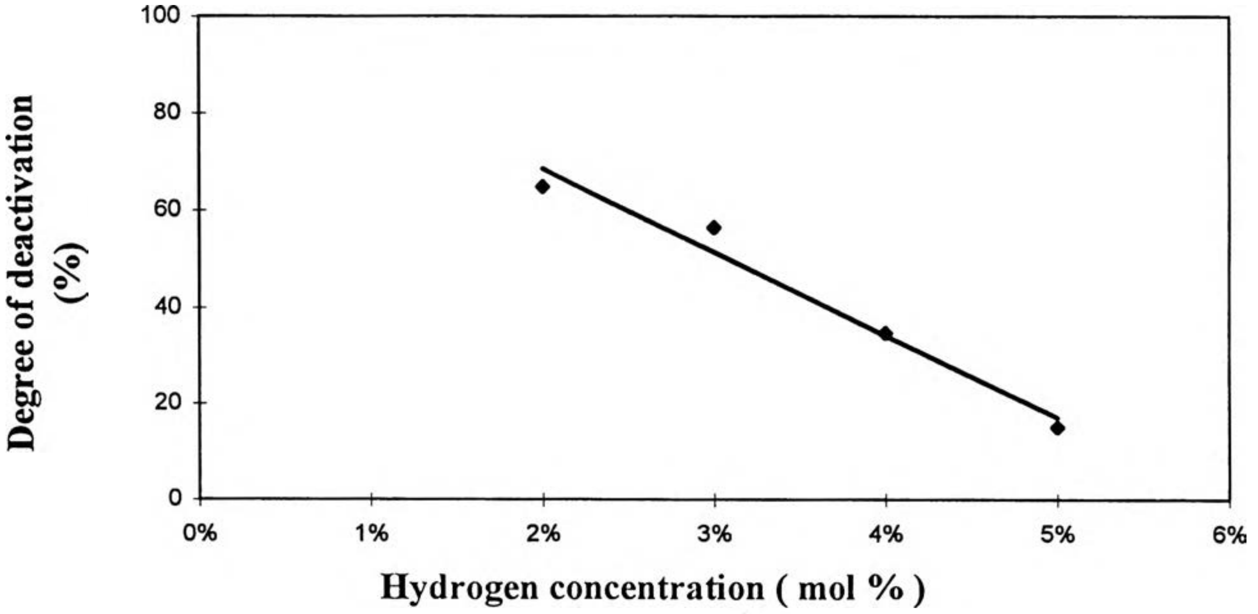

Figure 4.8 The relation between the degree of deactivation and hydrogen concentration for ethylene hydrogenation at 30 mol% ethylene and 80 °C.

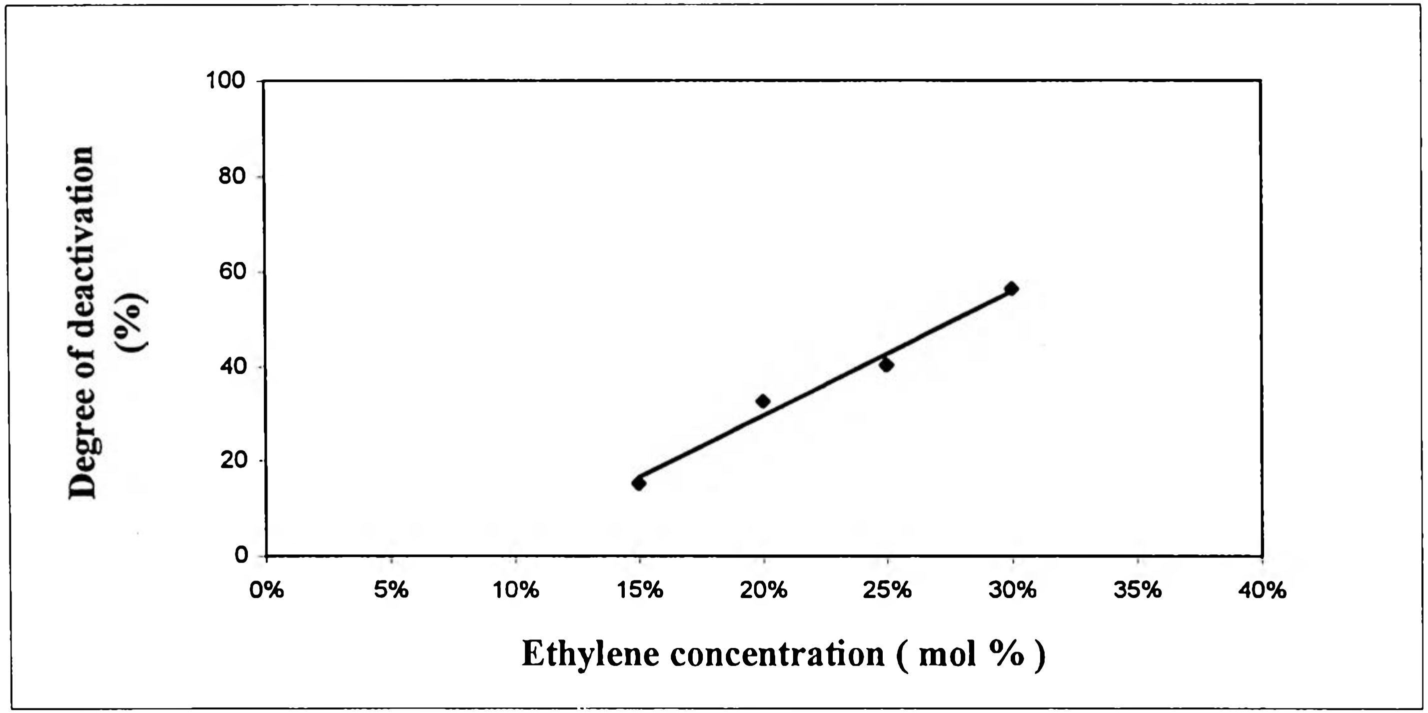

Figure 4.9 The relation between the degree of deactivation and ethylene concentration for ethylene hydrogenation at 3 mol% hydrogen and 80 °C.

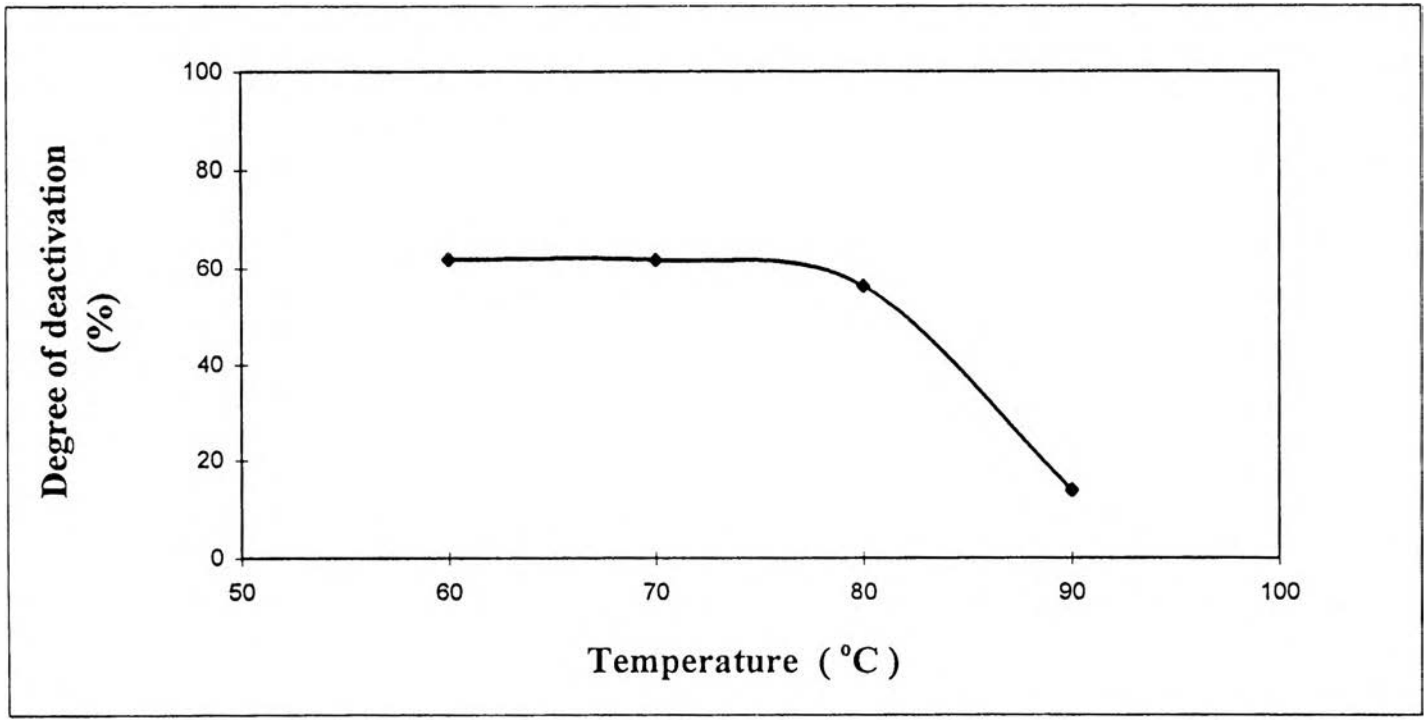

Figure 4.10 The relation between the degree of deactivation and temperature for ethylene hydrogenation at 3 mol% hydrogen and 30 mol% ethylene.

Table 4.1 The relative degree of deactivation and transient period for the ethylene hydrogenation experiments

Concentration		Temperture	Relative degree of deactivation	Transient period
Hydrogen (mol %)	Ethylene (mol %)	(^{o}C)	(%)	(min)
5	30	80	15	90
4	30	80	35	380
3	30	80	56	480
2	30	80	65	500
3	30	80	56	350
3	25	80	40	400
3	20	80	33	250
3	15	80	15	180
3	30	90	14	120
3	30	80	56	420
3	30	70	62	420
3	30	60	62	200

the catalyst lost 56% of its initial activity. However, at 90°C, a very different behavior was observed, and the catalyst lost only about 15 % of its initial activity. It can be seen that the shape of the deactivation curves at 90 °C and 60 °C are similar, that is the rates drop rapidly and then level off while the results at 70 °C and 80 °C show a more gradual and prolonged decrease in rate. Figure 4.10, the plot between the degree of deactivation and temperature, shows that the degree of deactivation remains almost constant at the temperature 60 - 80 °C and then drops sharply as the temperature increases to 90 °C. This may suggest that the reactions at 60-80 °C and at 90 °C occur via different deactivation mechanisms. The explanation for this might be the hydrogen regeneration of the carbonaceous deposit on the metal surface as shown in Cortright et al. (1991) 's work using Pt catalyst. At high temperature, they found that carbonaceous deposit can be removed by reaction with hydrogen. Thus, for the 90 °C case, it is conceivable that even on Pd-Ag catalysts the carbonaceous deposit blocking the surface may partly be removed by reaction with hydrogen, resulting in the low relative degree of deactivation. The temperature of 60-80 °C may not be high enough to achieve the hydrogen regeneration of the carbonaceous deposit on the catalyst.

From Figures 4.11, and 4.12, the order of reaction with respect to hydrogen and ethylene were 1.60 and -0.98, respectively. The apparent activation energy (E_a) was found to be 38 kJ/mol (Fig. 4.13). Although similar negative ethylene orders with a value close to -1 have been reported in the literature (Bos et al., 1993), it is surprising, given the fact that the ethylene concentration used in the experiments was high compared to the hydrogen concentration. As a result, ethylene adsorption should dominate the surface and one would expect an order close to zero. The observed negative order of ethylene is indicative of a competitive adsorption with hydrogen on the palladium surface. The results of this work suggest that the relative amounts of

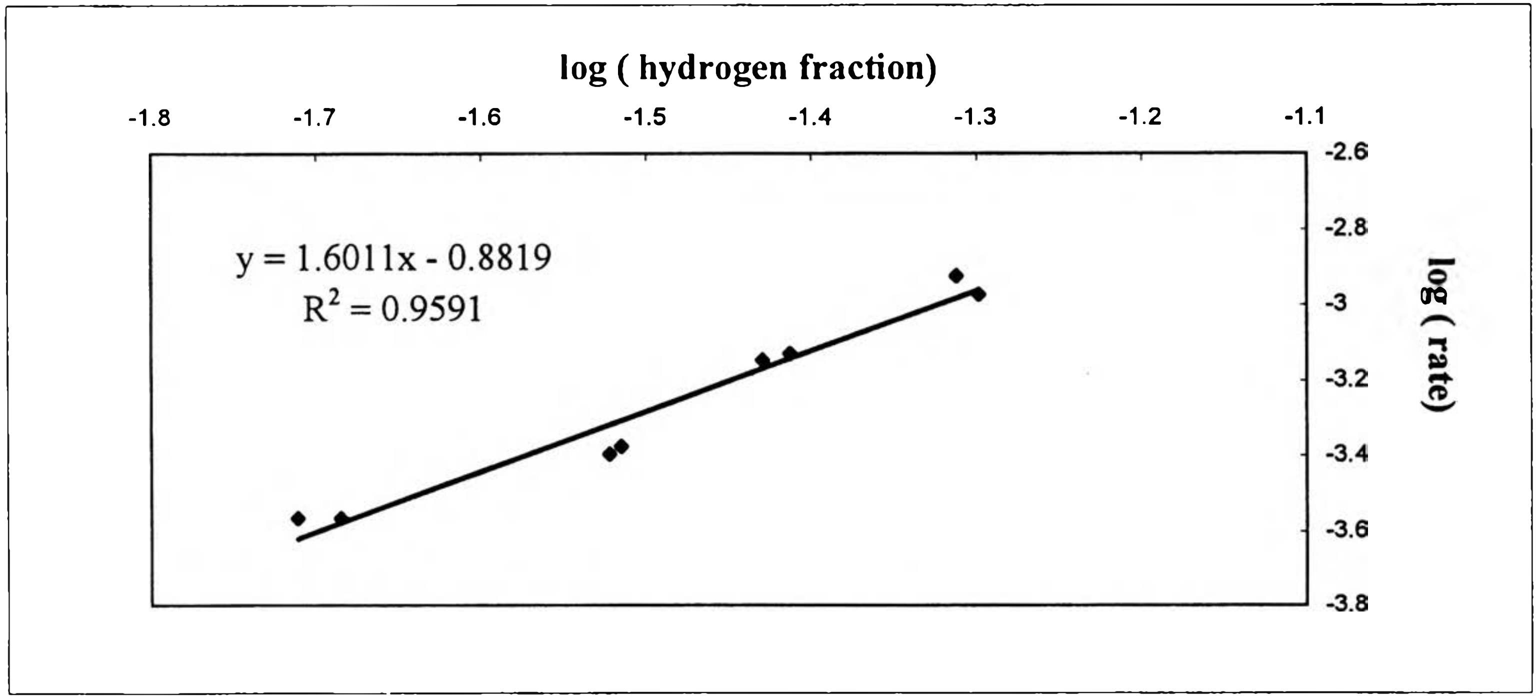

Figure 4.11 Hydrogen dependence of ethylene hydrogenation at 30 mol% ethylene and 80 °C.

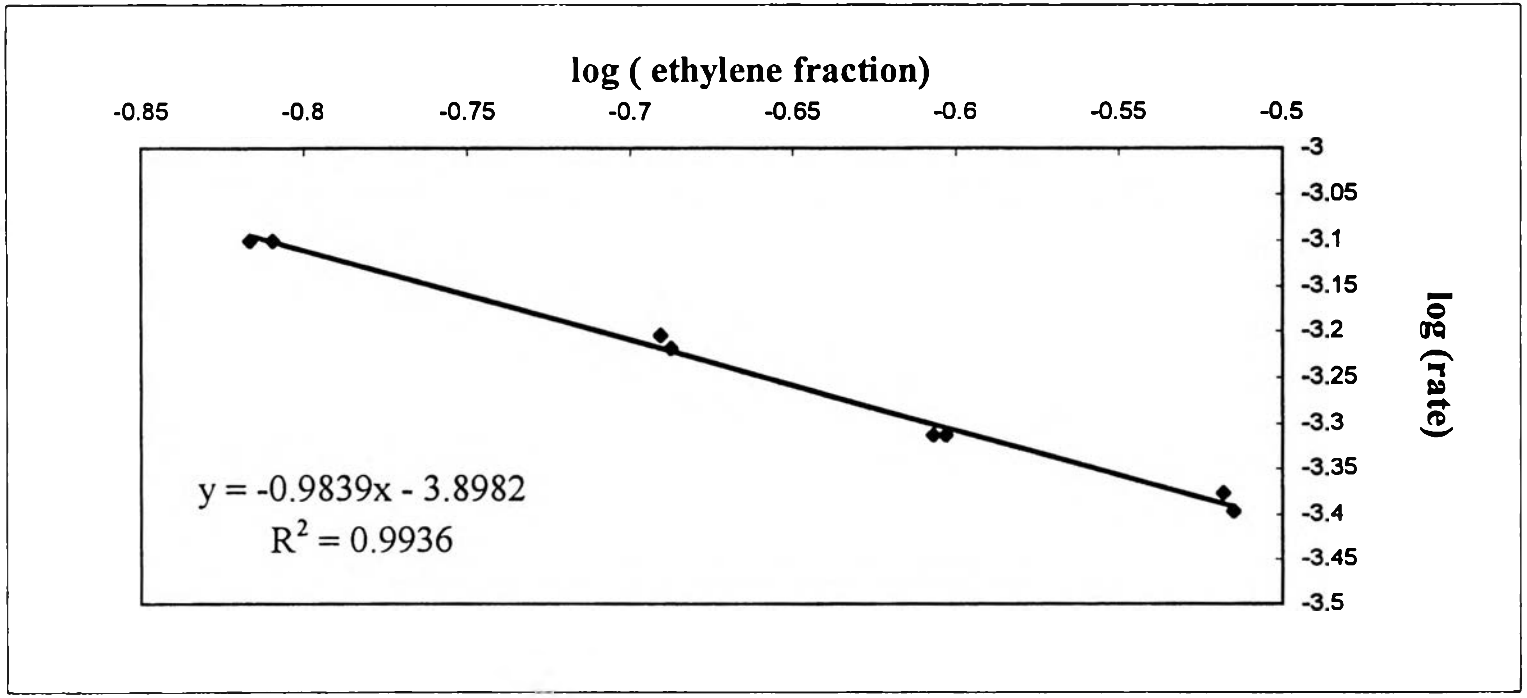

Figure 4.12 Ethylene dependence of ethylene hydrogenation at 3 mol% hydrogen and 80 °C.

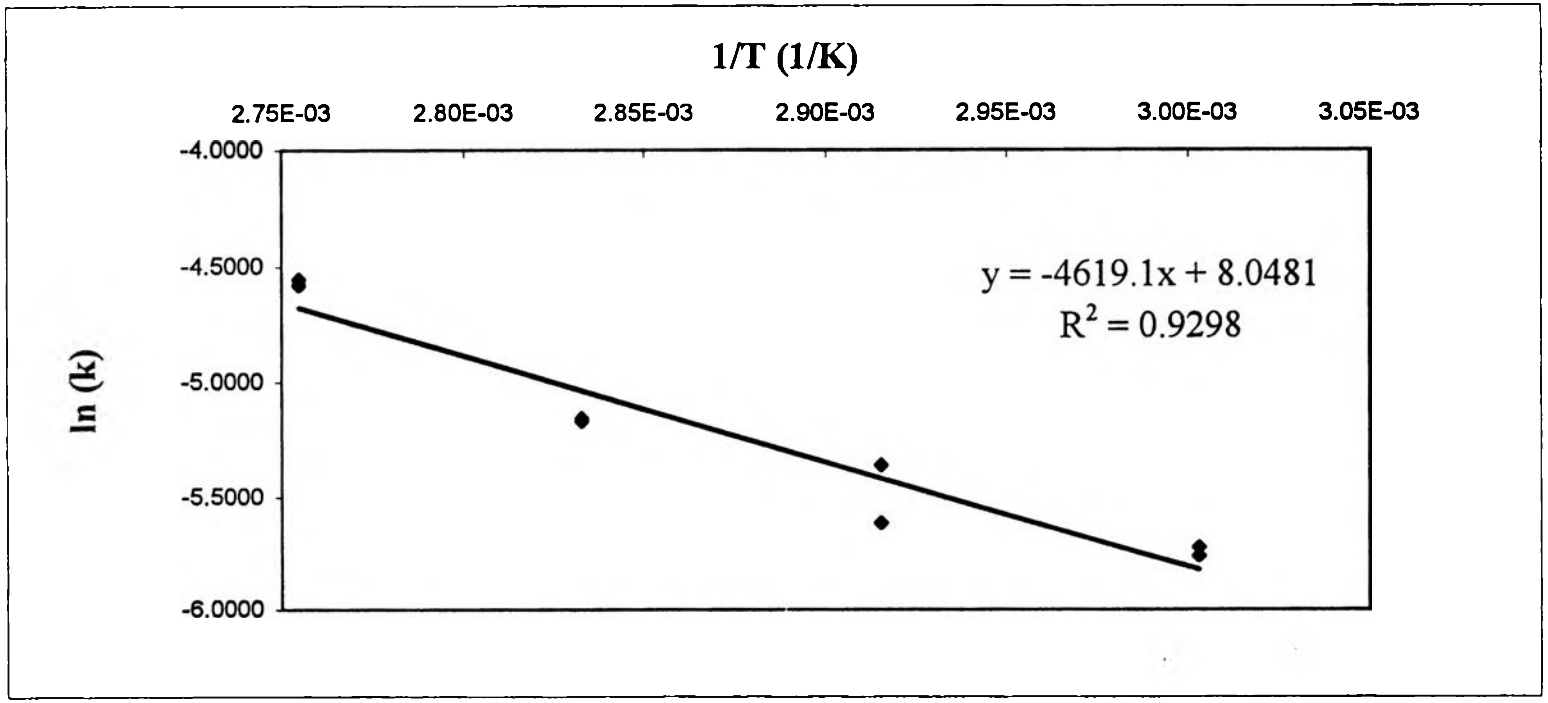

Figure 4.13 Arrhenius plot for ethylene hydrogenation experiment at 3 mol% hydrogen and 30 mol% ethylene.

adsorbed hydrogen and adsorbed ethylene were not much different, thereby permitting competitive adsorption to take place. The following two questions could help find explanations:

1. What could cause the hydrogen amount to be high enough to be competitive with ethylene?
2. What could cause the ethylene amount to decrease to be approximately close to that of hydrogen?

In answer to question 1, one could argue that ethylene may dissociatively adsorb on the Pd surface. The hydrogen atoms created in the dissociative adsorption step could then be added to the hydrogen pool available for reaction, thus increasing the total hydrogen amount involved in the reaction enough to compete with ethylene.

For question 2, the answer may be as follows: during the hydrogenation, carbonaceous deposits can be formed on the surface of the support as proposed by several authors (Cortright et al. (1991) and Zaera et al. (1983)). This carbonaceous layer is proposed to play an important role in this reaction since ethylene is presumed to adsorb on this layer and react with hydrogen spilled over from the Pd sites. The extent of spilled over hydrogen to the support is negligible for the clean surface, but may become significant once the surface is covered by the carbonaceous deposits. As a result, two pathways for hydrogenation of ethylene occur in parallel, i.e., the hydrogenation on the Pd surface and the reaction on the carbonaceous deposits on the support. The latter pathway would utilize the enhanced hydrogen transfer from the Pd surface induced by the formation of the deposits. Consequently, the amount of adsorbed ethylene on the Pd surface may not be high enough compared to that of hydrogen to dominate the Pd surface, and this would allow the competitive adsorption of hydrogen on the Pd surface.

The reaction rate expression is

$$r = 9.84e^{(38/RT)} (p_{ethylene})^{-0.98}(p_{hydrogen})^{1.60}$$

where

T is expressed in Kelvin,

and $p_{ethylene}$ and $p_{hydrogen}$ are expressed in kg /cm^2.

4.2.3 Kinetics studies of acetylene hydrogenation

The observed decrease of reaction rate from the initial value to a steady state, as can be seen in Figures 4.14, 4.15 and 4.16, is attributed to catalyst deactivation caused by carbonaceous deposits forming during the hydrogenation of acetylene. The final steady state activities for acetylene hydrogenation are reached much faster as compared to ethylene hydrogenation. Margitfalvi et al.(1981), studied acetylene hydrogenation on Pd black catalysts using a double isotopic labeling method and showed that no C4 oligomer came from ethylene. However, Cortright et al. (1991), who studied the ethylene hydrogenation on Pt, showed that the deactivation occurred by the blocking of active sites by carbonaceous deposits. From these two studies, it may be concluded that although ethylene hydrogenation contributes to the formation of carbonaceous deposits, it does so to a smaller extent and at a smaller rate compared to carbonaceous deposits formation from acetylene hydrogenation. Therefore, the formation of carbonaceous deposits from ethylene might not be detected during the hydrogenation of an acetylene-ethylene mixture. Furthermore, the formation of carbonaceous deposits formed from ethylene might be affected by the presence of acetylene. This might be an explanation for the faster deactivation rate of acetylene hydrogenation, compared to the more gradual deactivation of the ethylene hydrogenation.

It can be seen from Fig.4.17 that the degree of deactivation shows a general trend of decreasing levels of deactivation with an increase in hydrogen concentration. However, the trend is not smooth and the curve exhibits a fluctuation. At this point it cannot be ruled out that fluctuations in concentration or temperature at the beginning of some of the runs may have introduced experimental error. The overall trend may be the result of the competitive adsorption of acetylene with hydrogen. Figures 4.14, 4.15 and 4.16 and Table 4.2 show that, for each experiment, the rate decreases rapidly from the initial value and reaches the steady state at approximately 60 minutes after the start of the reaction, independent of hydrogen and acetylene concentrations and temperature. From Table 4.2 and Figure 4.18, it can be seen that the relative degree of deactivation is independent of acetylene concentration. However, it must be noted that the independence of deactivation on acetylene concentration may be due to the small range of acetylene concentration used in this work so that no significant changes in the degree of deactivation were observed. It is possible that experiments conducted at higher acetylene concentration would give higher degree of deactivation, since one would expect that the formation of the carbonaceous deposits is promoted by an increase in acetylene concentration in the gas phase. Similarly to Fig 4.10, Fig.4.19 shows a decrease in the degree of deactivation with an increase in temperature although, there is some scatter in the data. The explanation for this is similar to that stated in the ethylene hydrogenation, namely the hydrogen regeneration of the catalyst during the reaction. Since the regeneration is favored by high temperature, the extent of carbonaceous deposit is low, and this in turn, decrease the degree of deactivation as the temperature goes up.

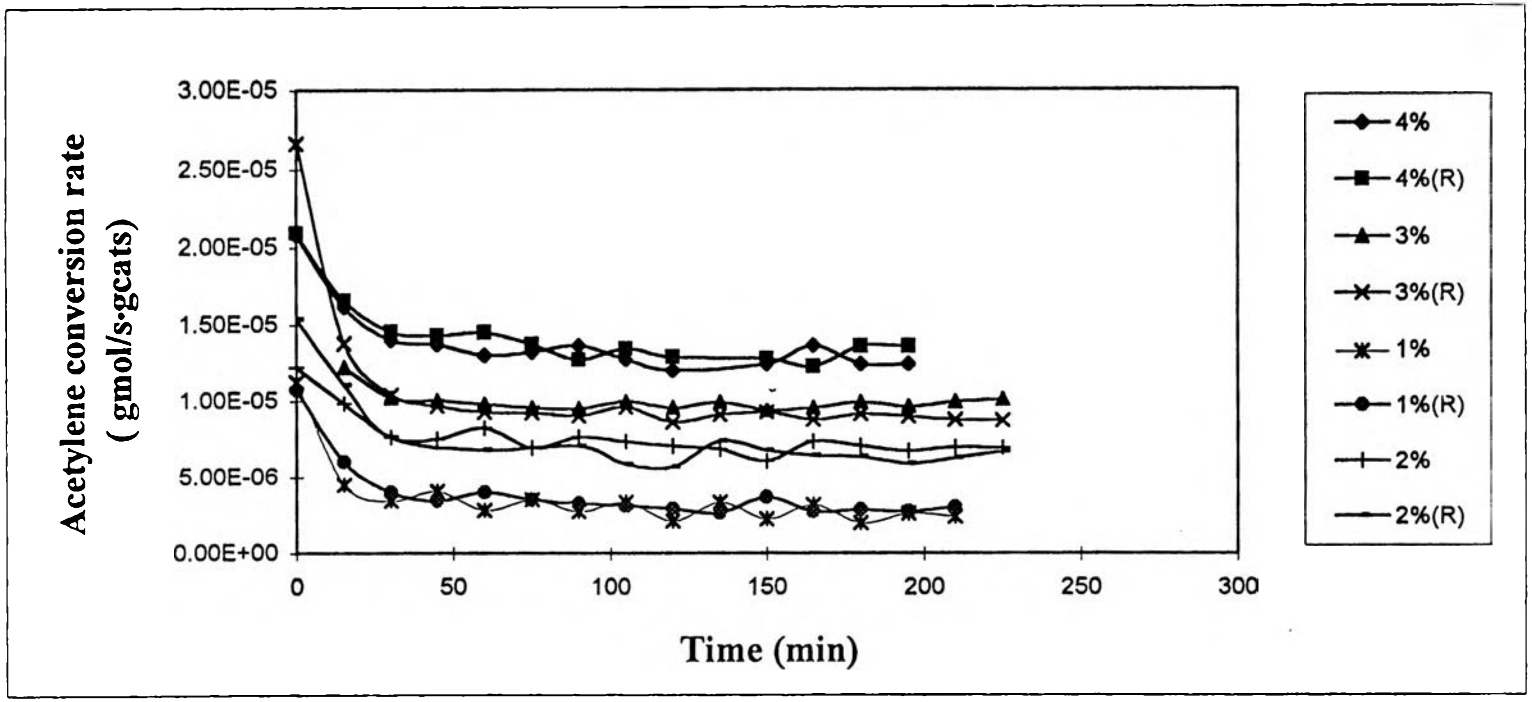

Figure 4.14 Deactivation curve for hydrogen dependence of acetylene hydrogenation experiments at 1 mol% acetylene and 80 °C.

Note : Hydrogen concentrations were shown in the legend. R denotes the repeating experiment.

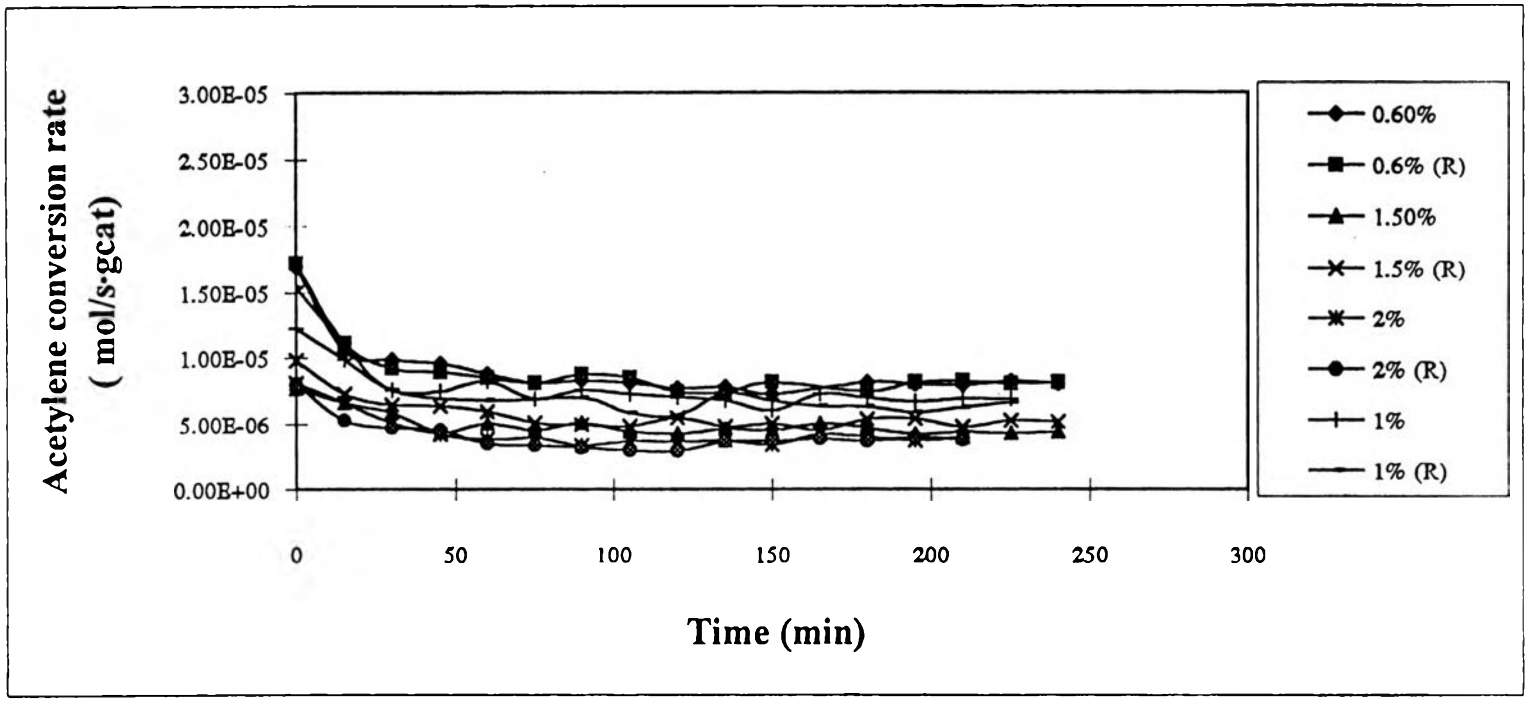

Figure 4.15 Deactivation curve for acetylene dependence of acetylene hydrogenation experiments at 2 mol% hydrogen and °80 C.

Note : Acetylene concentrations were shown in the legend. R denotes the repeating experiment.

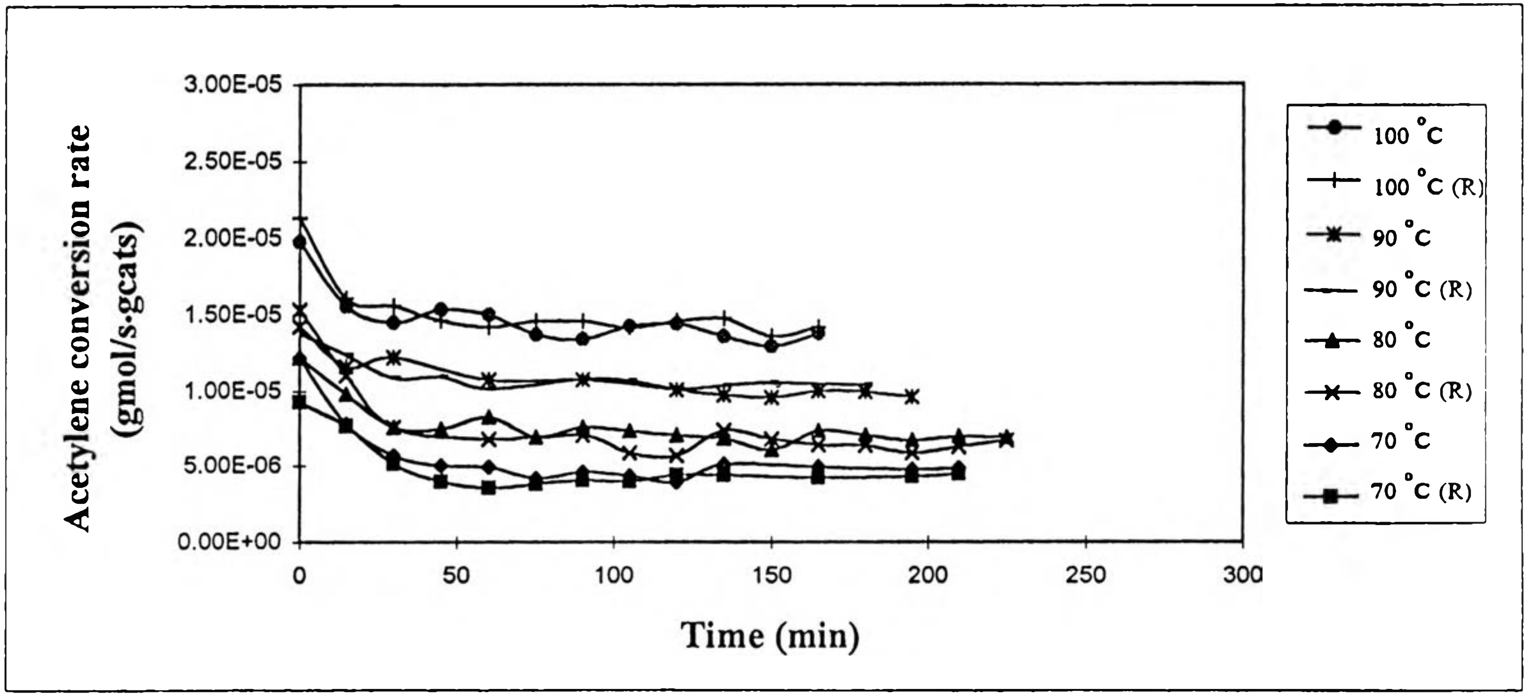

Figure 4.16 Deactivation curve for temperature dependence of acetylene hydrogenation experiments at 2 mol% hydrogen and 1 mol% acetylene.

Note : Reaction temperature were shown in the legend. R denotes the repeating experiment.

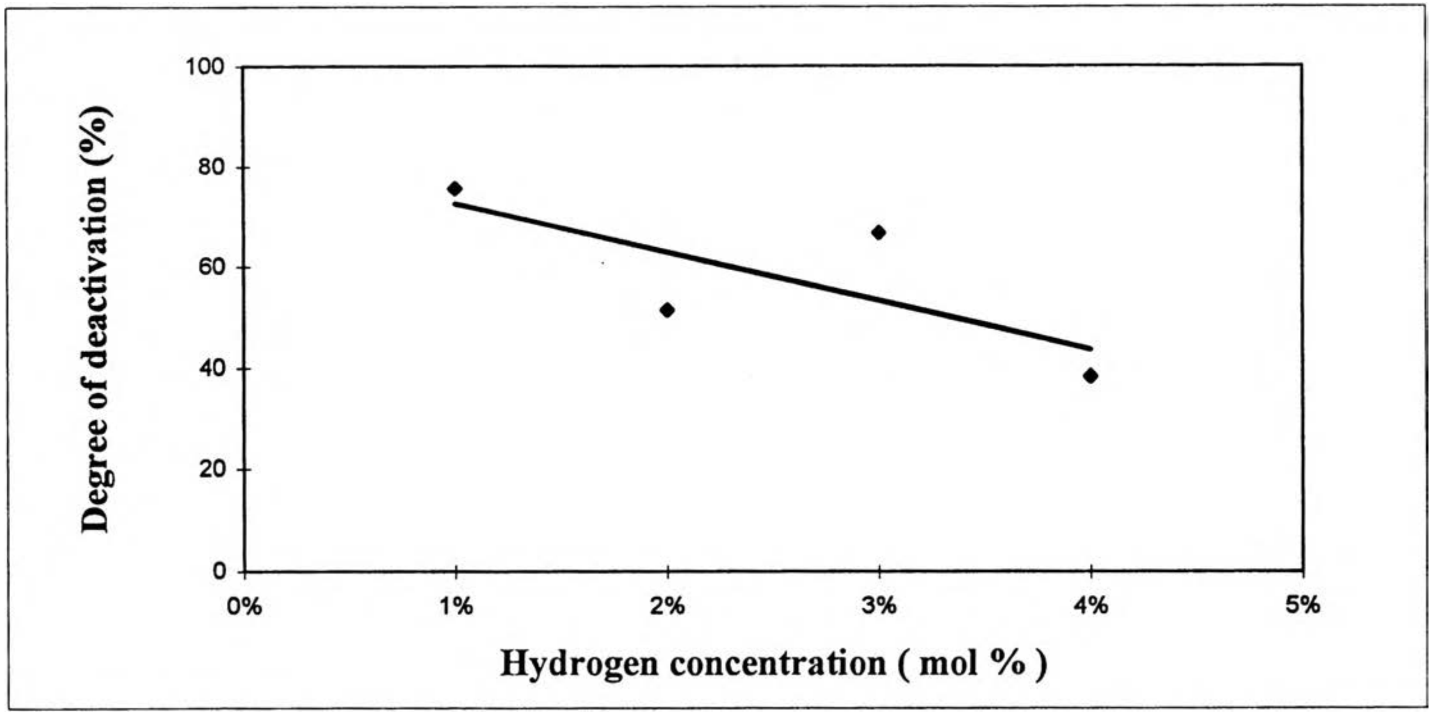

Figure 4.17 The relation between the degree of deactivation and hydrogen concentration for acetylene hydrogenation at 1 mol% acetylene and 80 °C.

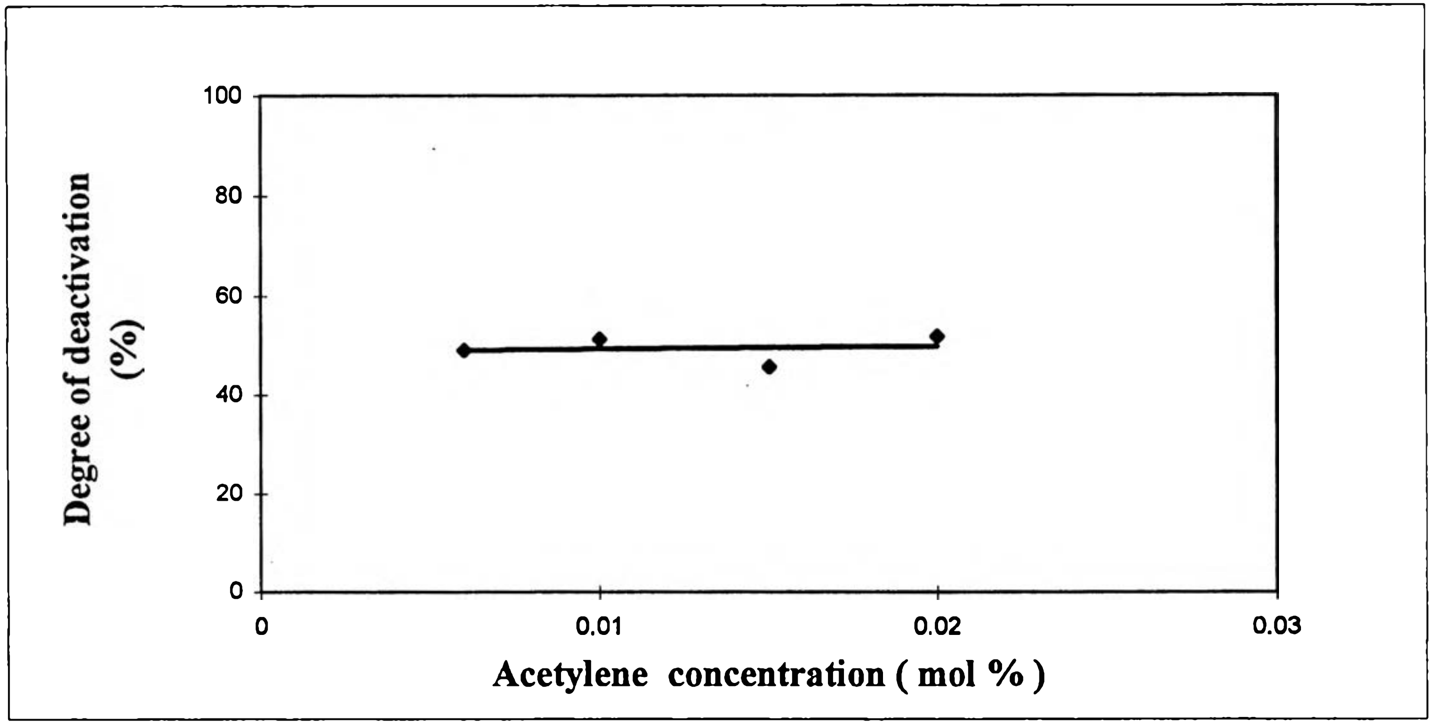

Figure 4.18 The relation between the degree of deactivation and hydrogen concentration for acetylene hydrogenation at 2 mol% hydrogen and 80 °C.

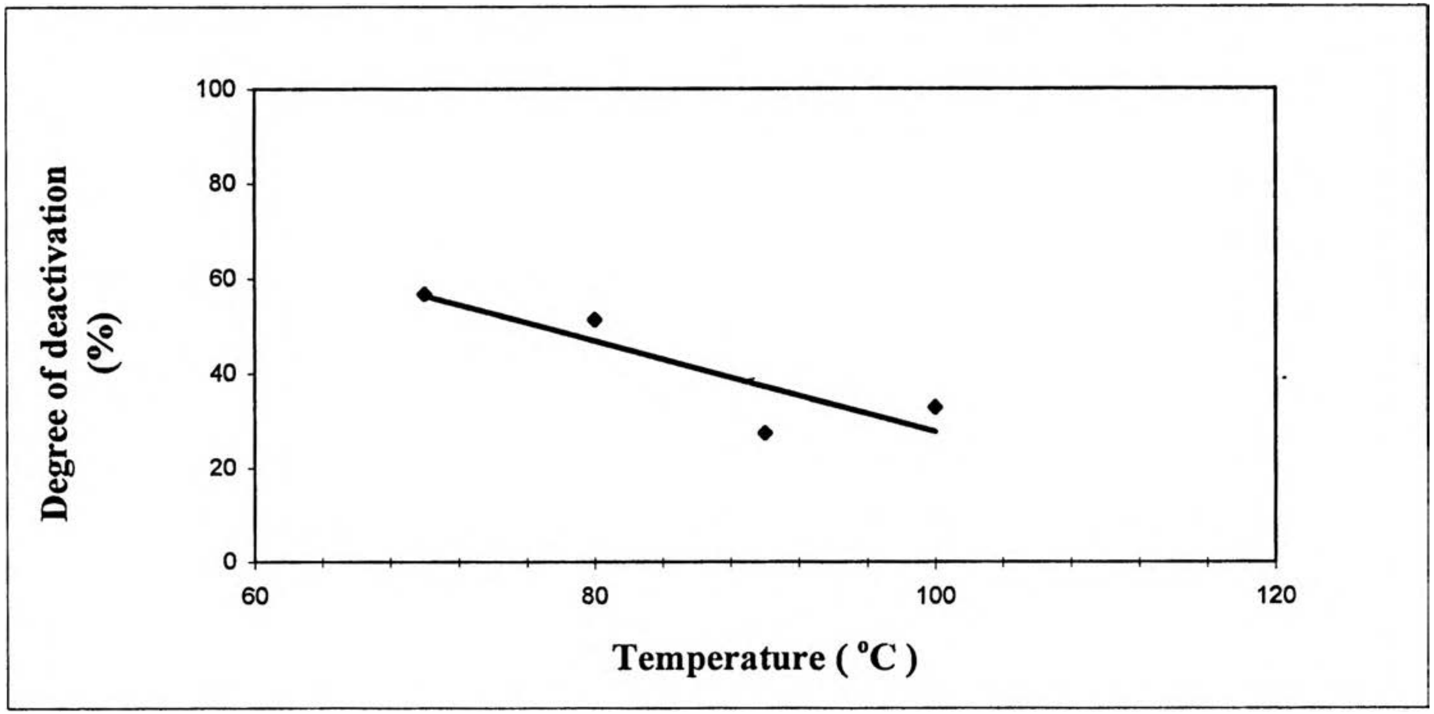

Figure 4.19 The relation between the degree of deactivation and temperature for acetylene hydrogenation at 2 mol% hydrogen and 1 mol% acetylene.

Table 4.2 The relative degree of deactivation and transient period for the acetylene hydrogenation experiments

Concentration		Temperture (°C)	Relative degree of deactivation (%)	Transient period (min)
Hydrogen (mol %)	Acetylene (mol %)			
4	1	80	38	60
3	1	80	67	60
2	1	80	51	60
1	1	80	76	60
2	2.0	80	52	60
2	1.5	80	46	60
2	1.0	80	51	60
2	0.5	80	49	60
2	1	100	33	60
2	1	90	28	60
2	1	80	51	60
2	1	70	57	60

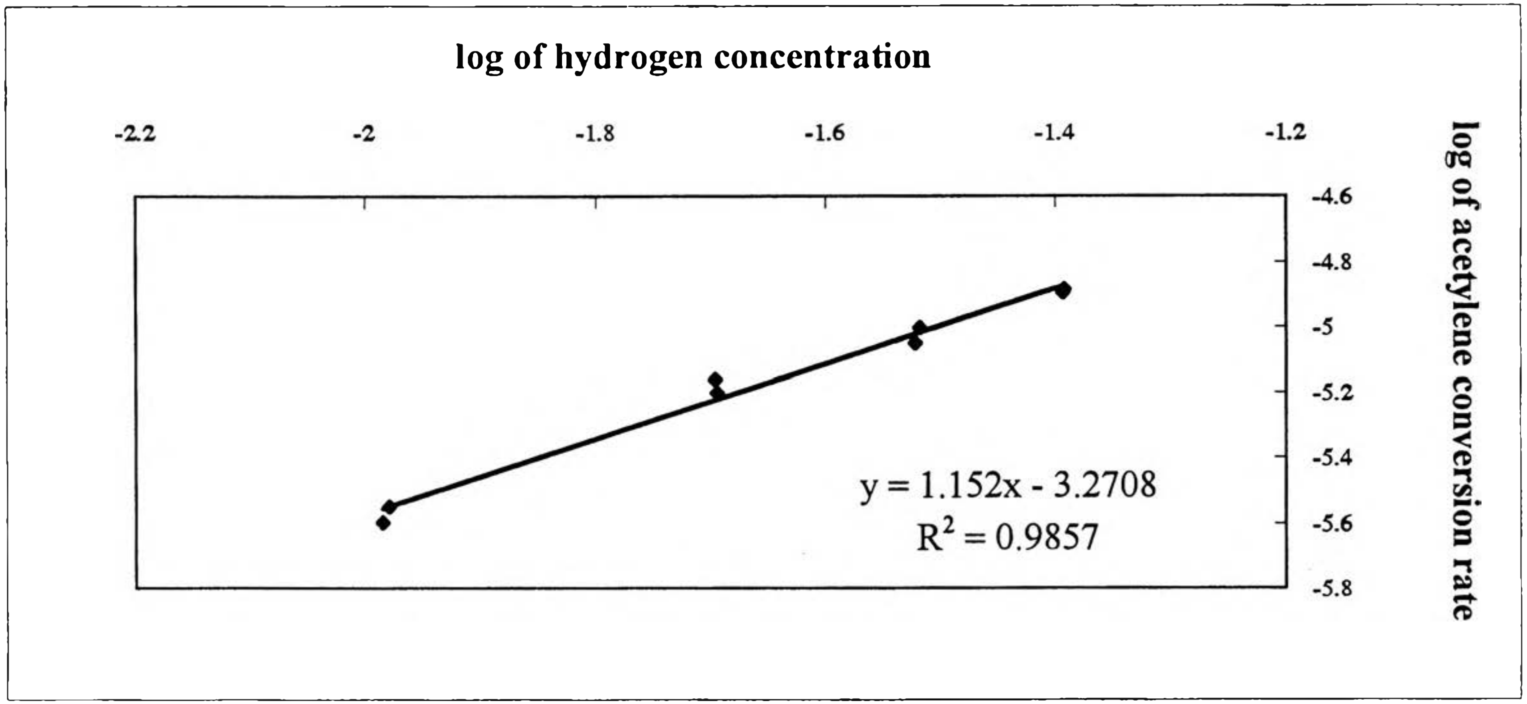

Figure 4.20 Hydrogen dependence of acetylene hydrogenation at 1 mol% acetylene and 80 °C.

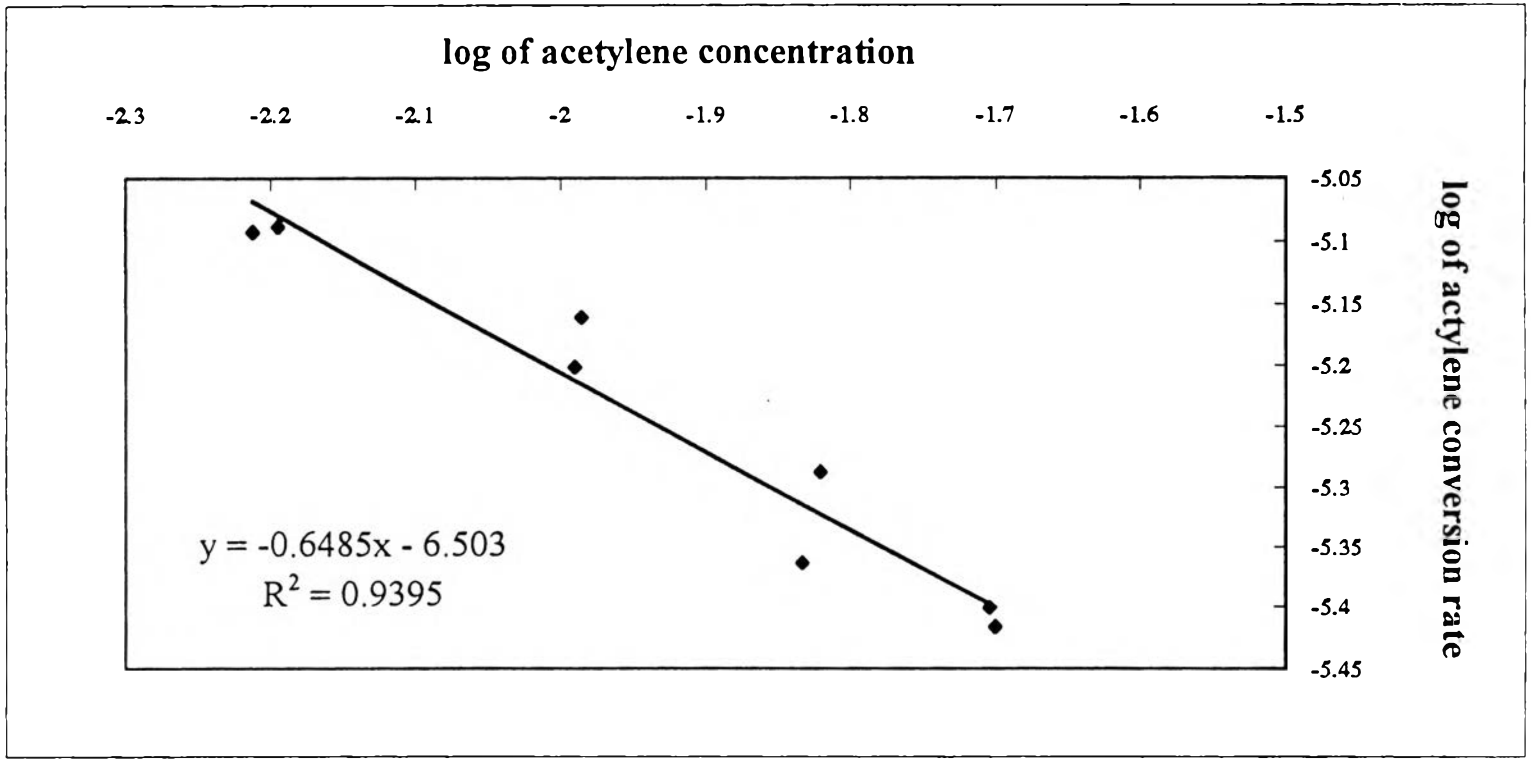

Figure 4.21 Acetylene dependence of acetylene hydrogenation at 2 mol% hydrogen and 80 °C.

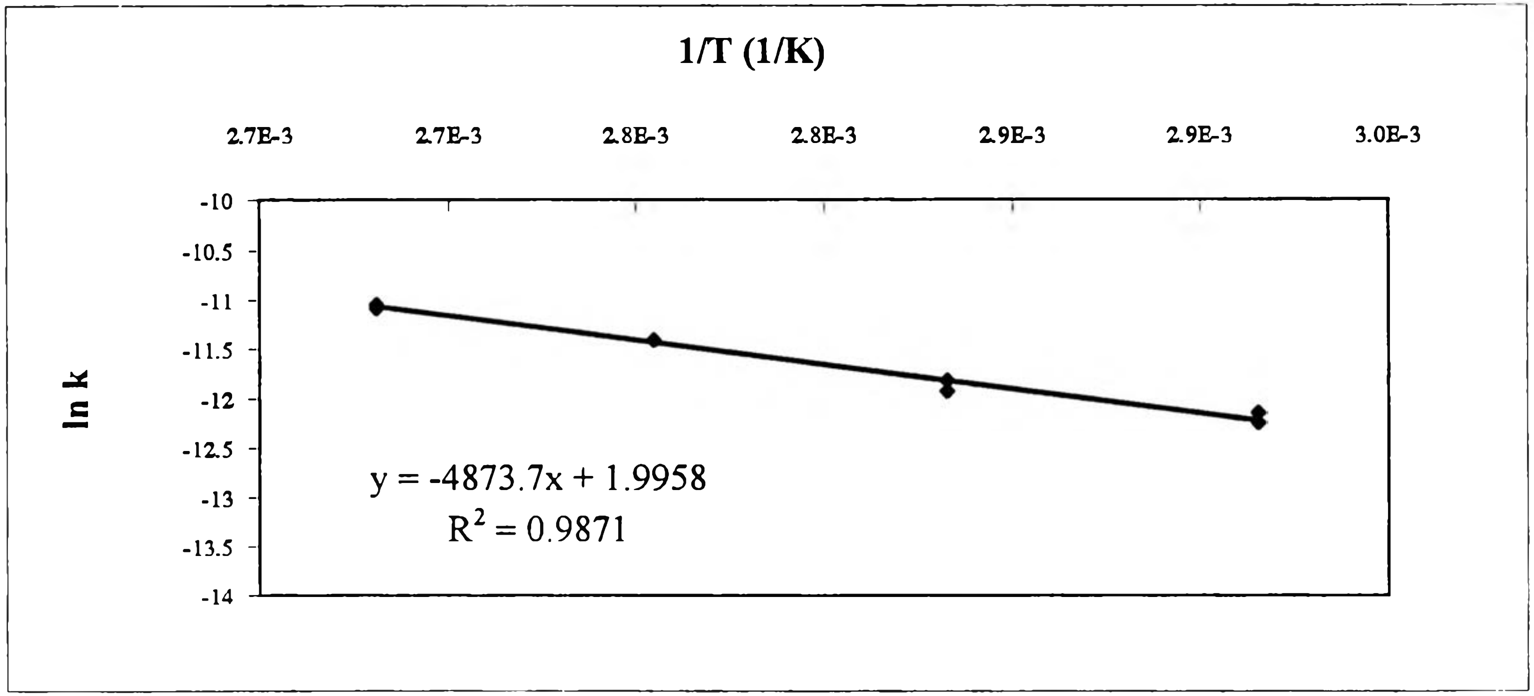

Figure 4.22 Arrhenius plot for acetylene hydrogenation experiments at 2 mol% hydrogen and 1 mol% acetylene.

The hydrogen order of 1.15 indicates that the adsorption of hydrogen is the rate determining step and the acetylene order of -0.94 indicates the competitive adsorption of acetylene with hydrogen on the Pd surface. In the experiments, the concentrations of hydrogen and acetylene were not much different from each other, thereby allowing the competitive adsorption of these two reactants.

The rate expression of acetylene hydrogenation is;

$$r = 1.99\, e^{(40/RT)}(p_{acetylene})^{-0.65}\,(p_{hydrogen})^{1.15}$$

where

T is expressed in Kelvin,

and pacetylene and phydrogen are expressed in kg /cm^2.

Comparison of kinetic order and activation energy among this work and the other's

Table 4.3 shows that the apparent activation energy for ethylene hydrogenation obtained from this work is in agreement with those obtained from the work of Bos et al.(1993), Cortright et al.(1991)and Zaera et al.(1983) For acetylene hydrogenation, the activation energy reported by Bos et al. (1993), Moses et al. (1983) are in close agreement with this result. When compared to these values, the apparent activation energies reported by Gva et al. (1988) and Aduriz et al. (1989) are rather high.

In general, the hydrogen orders reported tend to be approximately unity for both ethylene and acetylene hydrogenation. For ethylene hydrogenation, the orders are reported to depend on the temperature of reaction (Cortright et al.. 1991) varying from 0.55-1.04 in the temperature range of 223-336 K. The explanation for this might be that the rate of hydrogenation of half-hydrogenated species increases more rapidly with temperature than the rate of hydrogen adsorption and desorption. This may be the reason for the rather large range of values for the order obtained form various works since the temperature range used in each study was different. For acetylene hydrogenation, the hydrogen order reported in Bos et al. (1993) work are only 0.43 which is not in agreement with those obtained from other authors.

The ethylene orders are reported to be -0.98 to approximately zero except the result from Margitfalvi et al. (1981) who presented a possitive value. The acetylene orders shown in the table are either negative or zero except for the value obtained by Bos et al. (1993).

Since Bos et al. (1993) conducted the ethylene hydrogenation and acetylene hydrogenation separately as done in this work, it is useful to compare the result of these two works. The result for ethylene hydrogenation are in close agreement, but the results in acetylene hydrogenation in the absence of ethylene are different. Bos et al. (1993) showed two rate expressions, one for ethylene formation and the other for ethane formation. Typically, for commercial catalysts, the amount of ethane produced from acetylene (i.e., the further hydrogenation of ethylene produced from acetylene), can be neglected so only the formation of ethylene should be taken as the rate of acetylene conversion. However, according to the work of Bos et al. (1993) the formation of ethane could not be neglected. This may have caused their rather low hydrogen and acetylene orders shown in the proposed rate expression. It also may be the result of heat transfer limitations as stated in their work.

Table 4.3 The summary of kinetics data

Catalyst	Order			Temperature range (K)	Partial pressure range	Reference	Activation energy (Ea)	Comment
	Hydroen	Ethylene	Acetylene					
1. Pd black	1st up to someP_{H_2}	possitive	change from possitive to negative	273	D_2 0-5kP C_2H_2 0-0.8 kP C_2H_4 0-2.5 kP	Margitfalvi et al. .(1981)	-	Deuterium used
2. 0.04 wt% Pd / Al_2O_3	Not reported as nth kinetic order			303-343	H_2 4-16 kPa	Gva et al. (1988)	50+/- 4 kJ/mol	-
3.Pd on graphite plate	1	-	-	273-323	H_2 = C_2H_2 = 0.67 torr	Takasu et al. .(1985)	k=2E+17 molecule/cm^2*s	-
4. Pd / Al_2O_3	1.3-1.6	-	-0.5-0	273-313	H_2 9.9 Mol % C_2H_2 0.19-0.98 C_2H_4 42-77	Aduriz et al. .(1989)	67.42 kJ/mol	-
5. Pd / Al_2O_3	1.45 0.43	-0.85	0.52	303-353	H_2 2-15 vol %	Bos et al. (1993)	40 kJ/mol	Ethylene hydrogenation Acetylene hydrogenation
6. Pt	0.5-1.1	-0.7-0	-	233-333	H_2 6-90 kPa C_2H_4 0.67-10	Mikrokinetic of Heterogeneous catalyst .(1993)	-	Low T and high P high T and low P
7. Pt/silica Pt wire	1-0.5	0 to negative	-	223-336	H_2 50-650 torr C_2H_4 5-600 torr	Cortright et al. .(1991)	36.12 kJ/mol	-

Table 4.3 The summary of kinetics data (continued)

Catalyst	Order			Temperature range (K)	Partial pressure range	Reference	Activation energy (Ea)	Comment
	Hydroen	Ethylene	Acetylene					
8. 0.04 wt% Pd / Al_2O_3	> 1	0	0	-	H_2 1.5 - 7.5 kPa	Moses et al. .(1983)	41.8 kJ/mol	-
9.Pt-Pumice PT foil Colloidal Pt 3wt % of Pt / Al_2O_3	1.2	-0.5	-	-	H_2 20-200 mm C_2H_4 20-300mm	G.C. Bond et al (1956)	-	-
10. 10 Wt% Pd / Al_2O_3	0.84-0.93	.-0.3-0	-	-	H_2 0.05-0.4 toor C_2H_4 0.04-0.4 torr	Beebe et al. .(1985)	-	-
11. Pt(111) single crystal	1.31	0.6	-	300-370	H_2 10-100 torr C_2H_4 10-20 torr	Zaera et al. .(1983)	45.36 kJ/mol	-
12. 0.04 wt% Pd / Al_2O_3	1.15	-	-0.65	343-373	H_2 1-4 mol % C_2H_2 0.6-2 mol%	This work	40 kJ/mol	Acetylene hydrogenation
	1.6	-0.98	-	333-363	H_2 2-5 mol% C_2H_4 15-30 mol%	This work	38 kJ/mol	Ethylene hydrogenation