

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Reaction Studies

4.1.1 External Limitation

The acetylene conversion rate was plotted against the feed stream flow rate as shown in Figure 4.1. The curve becomes horizontal at approximately 300 ml/min. It is clear that the region of flow rate that has no external limitation starts at 300 ml/min. In this work, because of the lower limit in flow rate range of mass flow controllers used, the total flow rate of 350 ml/min was used for all of the experimental runs.

4.1.2 Acetylene Hydrogenation

Figures 4.2 and 4.3 illustrate that, for each experiment, the acetylene conversion rate decreases rapidly from the initial value and attains a steady state after about 60 minutes, independent of total flow rate and acetylene concentration. This decreasing rate is ascribed to catalyst deactivation because of carbonaceous deposits forming during the hydrogenation of acetylene.

It can be seen from Figure 4.4 that the degree of deactivation, calculated from Figure 4.3 increases with an increase in acetylene concentration. It is clear that the higher acetylene concentration, the higher degree of deactivation, since the formation of the carbonaceous deposits is promoted by an increase in acetylene concentration.

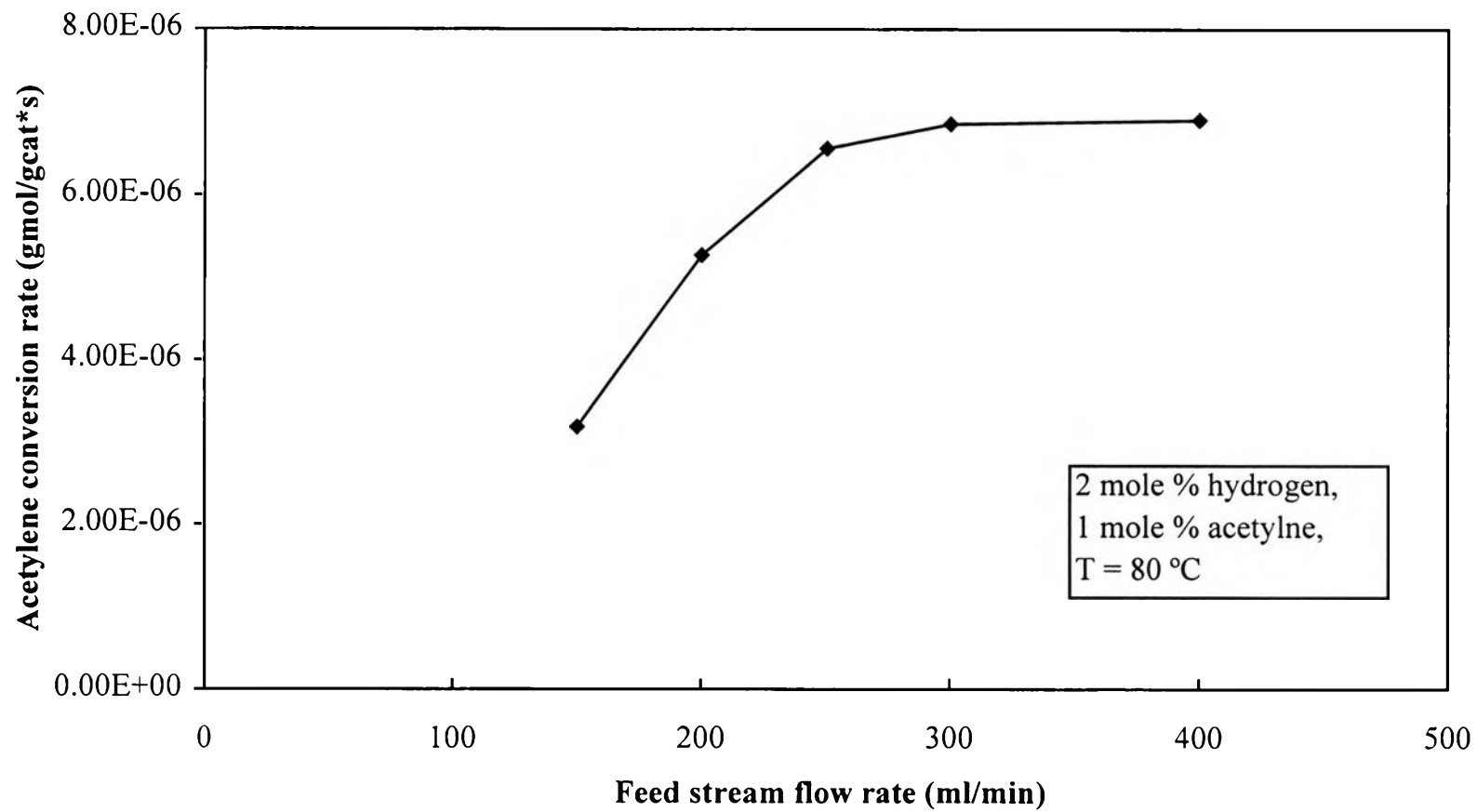


Figure 4.1 The test of external limitation for acetylene hydrogenation.

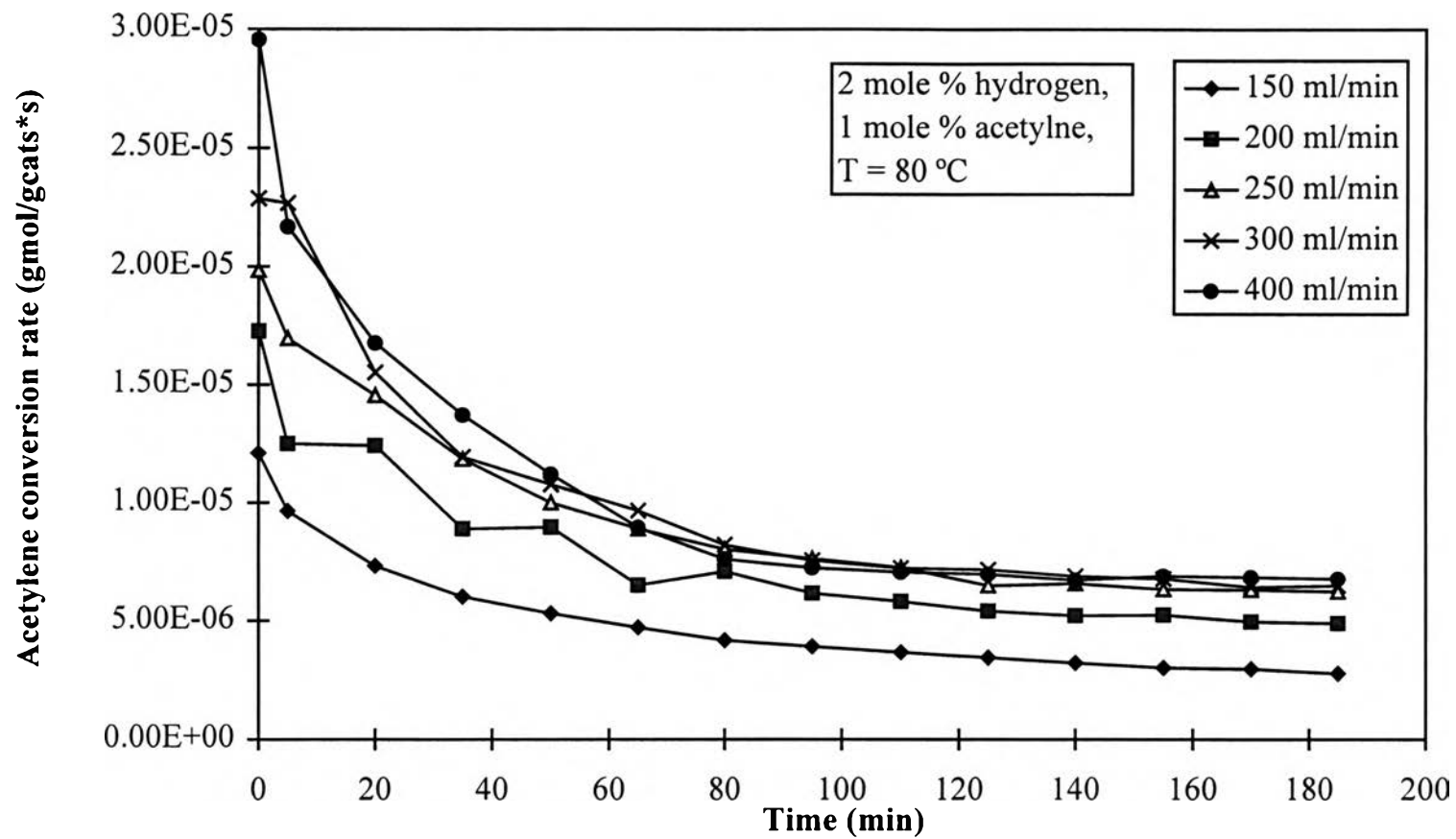


Figure 4.2 Deactivation curve for total flow rate dependence of acetylene hydrogenation.

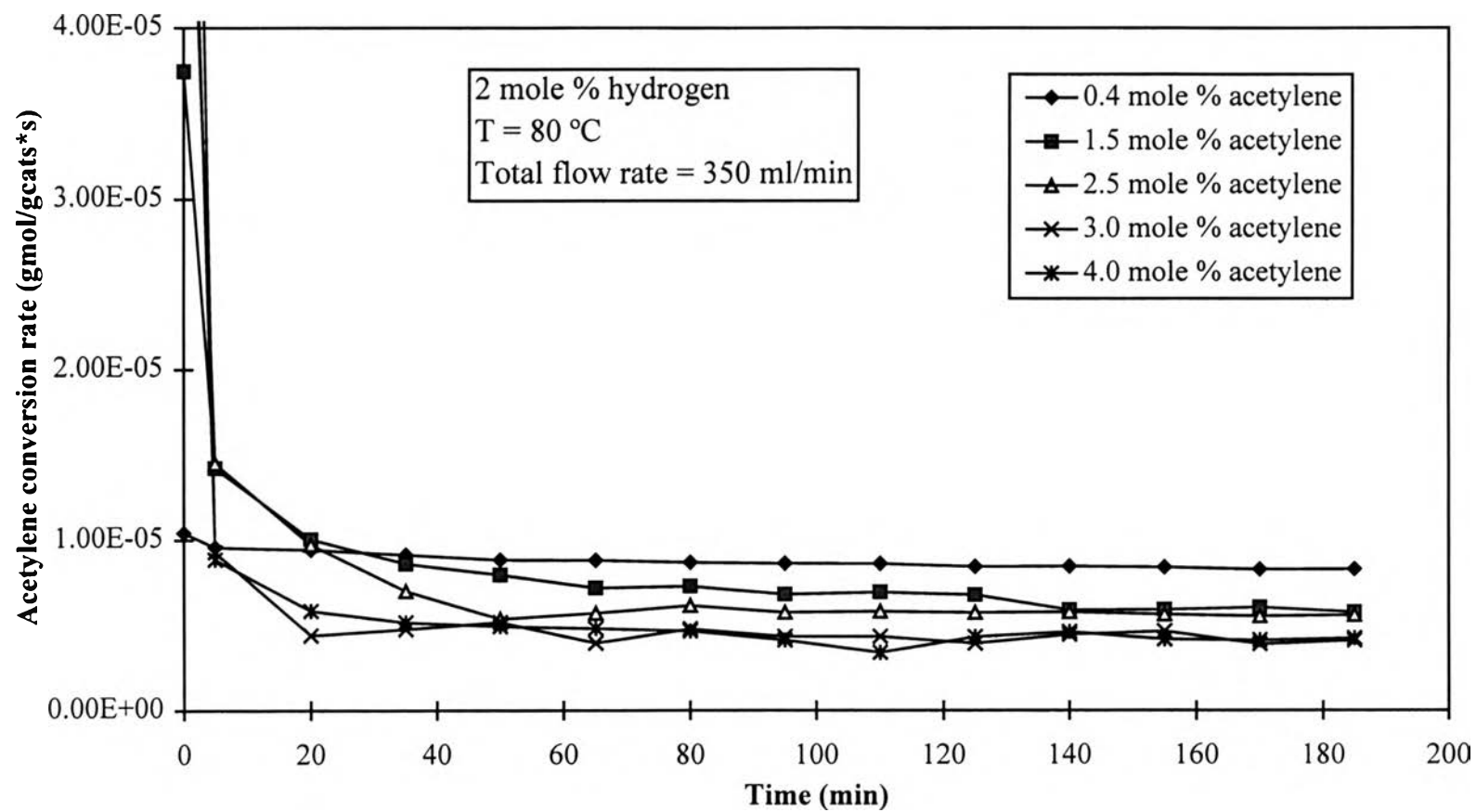


Figure 4.3 Deactivation curve for acetylene dependence of acetylene hydrogenation.

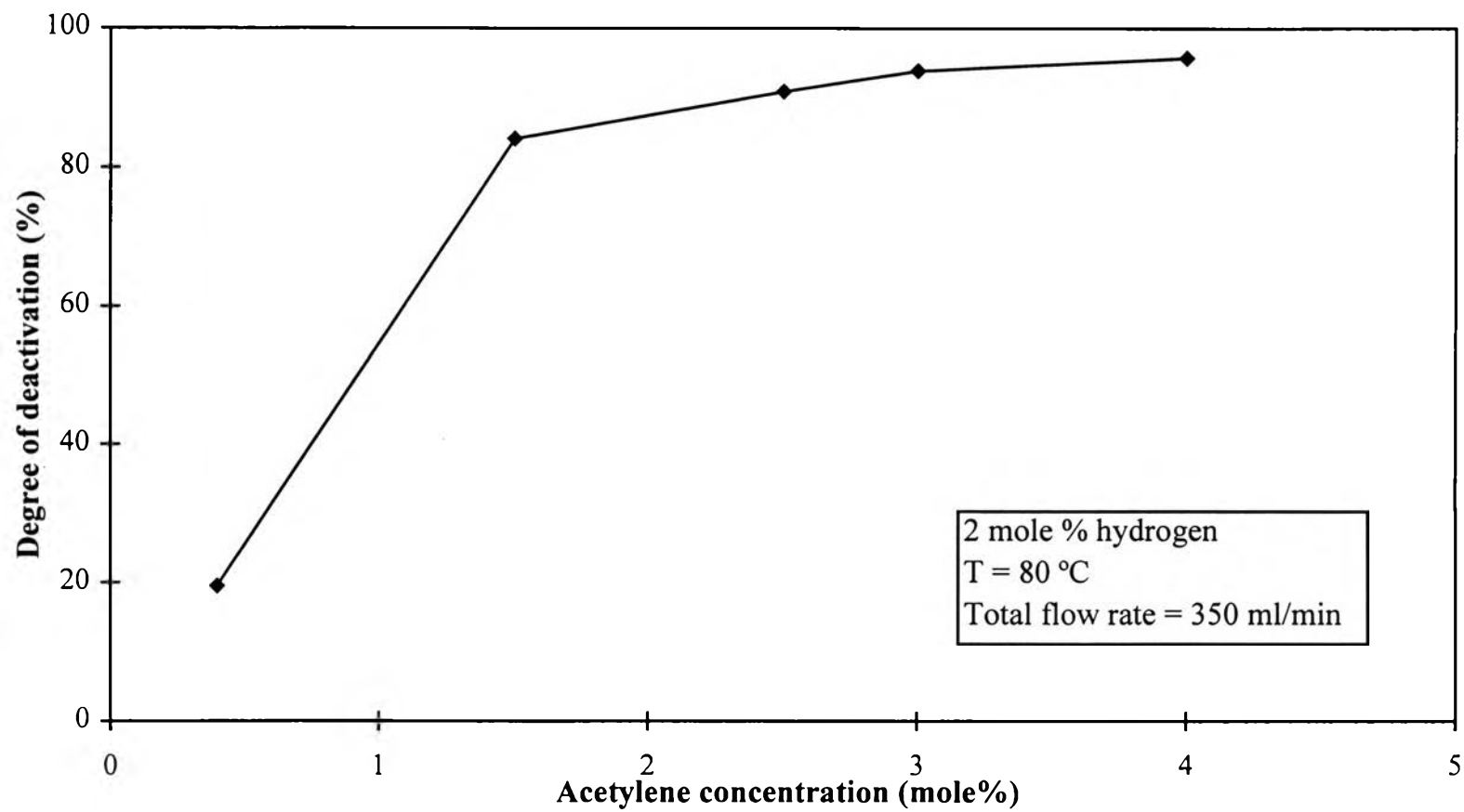


Figure 4.4 The relation between the degree of deactivation and acetylene concentration.

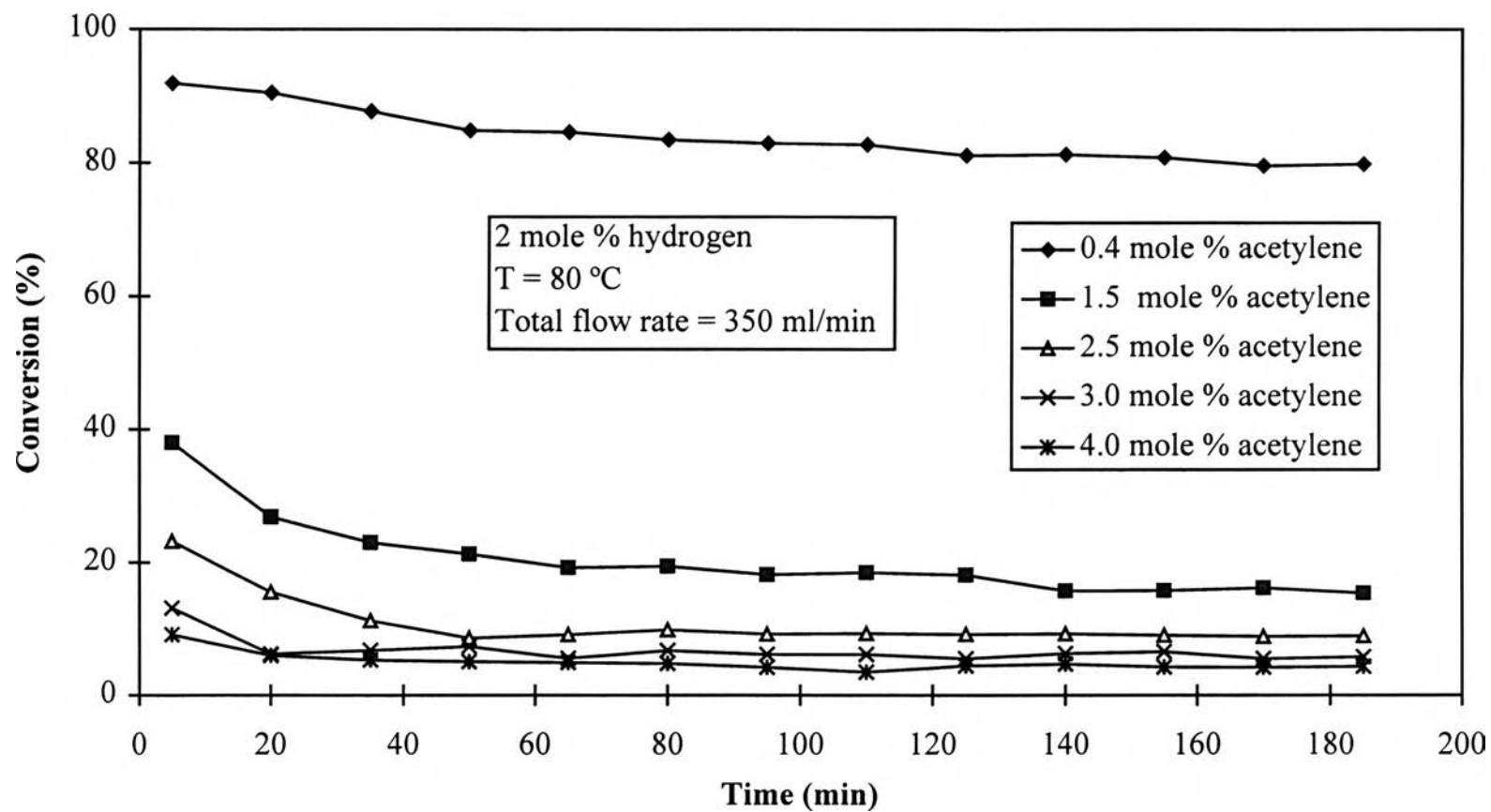


Figure 4.5 Conversion curve for acetylene concentration dependence of acetylene hydrogenation.

The conversion, shown in Figure 4.5, decreases with an increase in acetylene concentration. This is because at low acetylene concentration, most of acetylene is reacted, the conversion is high. But at high acetylene concentration, there is some acetylene remaining, the conversion is low.

4.1.3 Acetylene Hydrogenation in the Presence of Ethylene

Figure 4.6 shows the effect of acetylene concentration on the catalyst selectivity. At high acetylene concentration, the selectivity is nearly 100 %. From Bond et al. (1962)'s work, acetylene can be adsorbed stronger than ethylene. As a result, in acetylene/ethylene mixtures the hydrogenation of acetylene to ethylene is the main reaction, the direct hydrogenation reaction of acetylene to ethane is so small (LeViness et al., 1984).

4.2 **Temperature Programmed Desorption (TPD)**

The TPD experiment was performed over the temperature range of 40-600 °C. The Pd-Ag/ Al₂O₃ catalyst was first reduced in the stream of pure hydrogen at 200 °C and then was exposed to 55 ml/min of hydrogen at room temperature. TPD experiments were conducted by heating the sample in a stream of pure nitrogen at a heating rate of 10 °C/min. The obtained spectra (Figures 4.7 and 4.8) show two broad peaks. The first peak starts at the temperature of around 40 °C and ends at 220 °C. At higher temperatures, a second broad peak starts to develop, and even at 600 °C. It was observed that hydrogen still came off the sample. This suggests that under the experimental conditions, some of the hydrogen might not completely desorb from the palladium surface even at 600 °C.

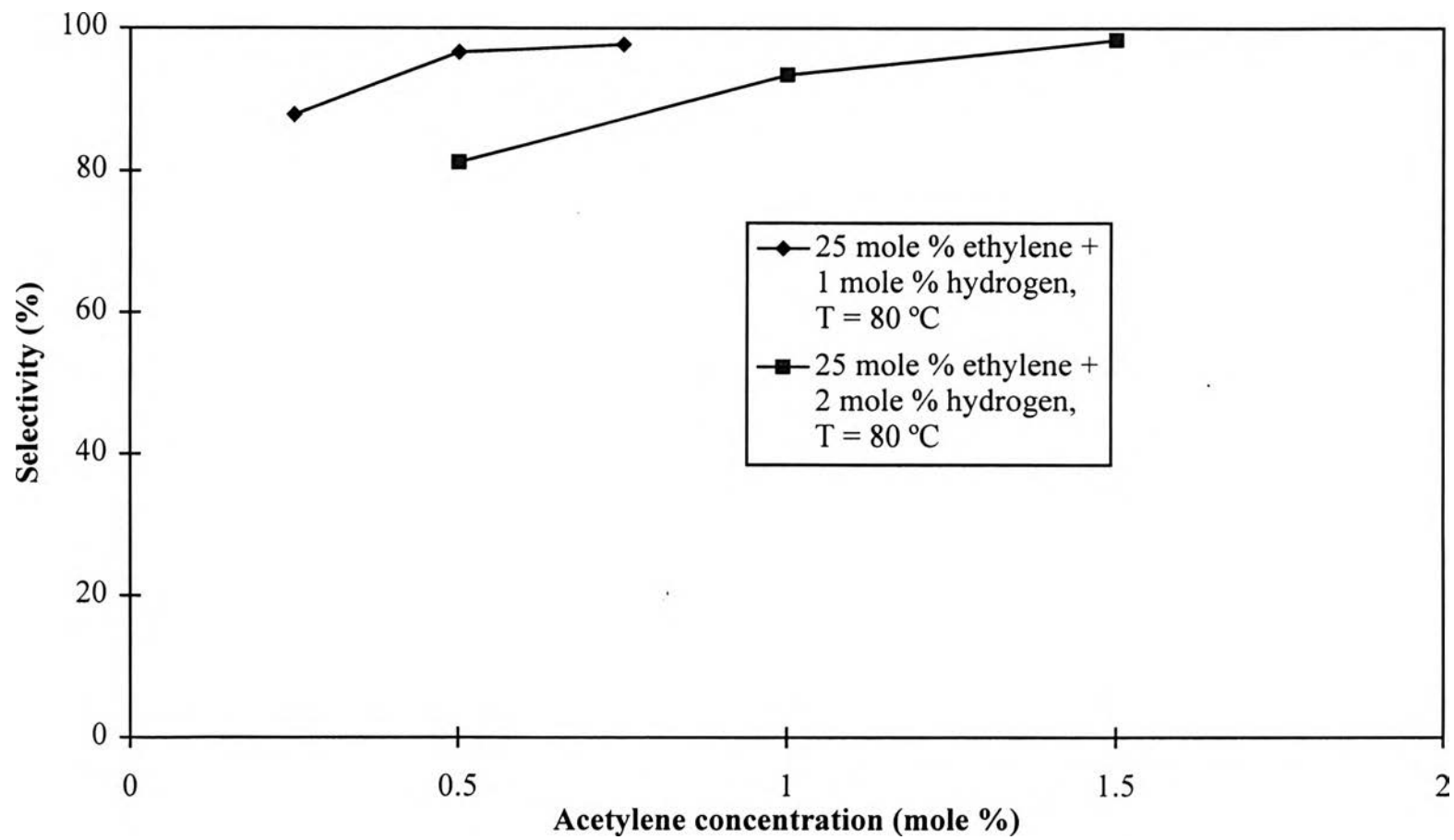


Figure 4.6 The selectivity versus acetylene concentration.

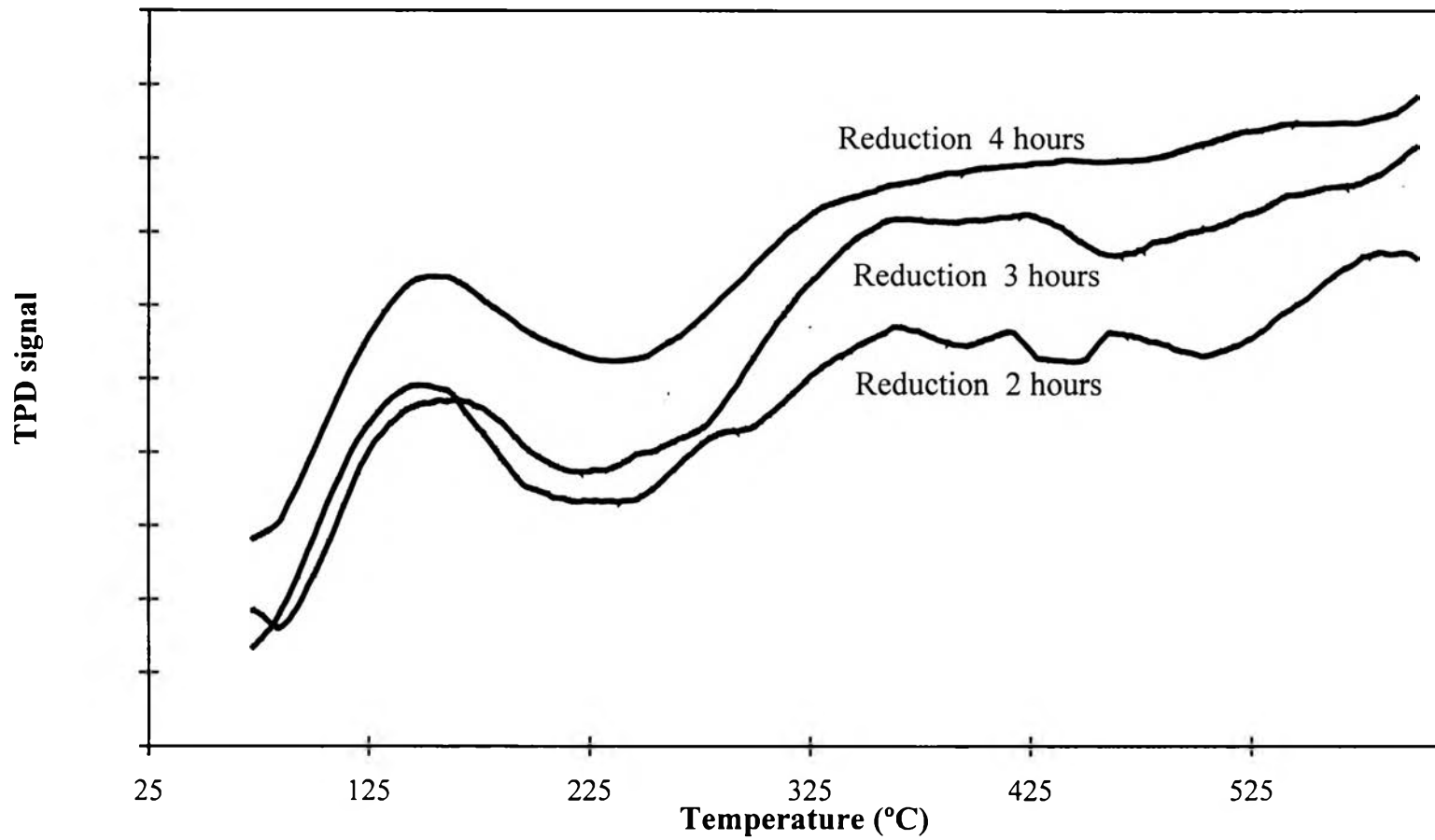


Figure 4.7 The temperature programmed desorption curve at 15 minutes exposure time.

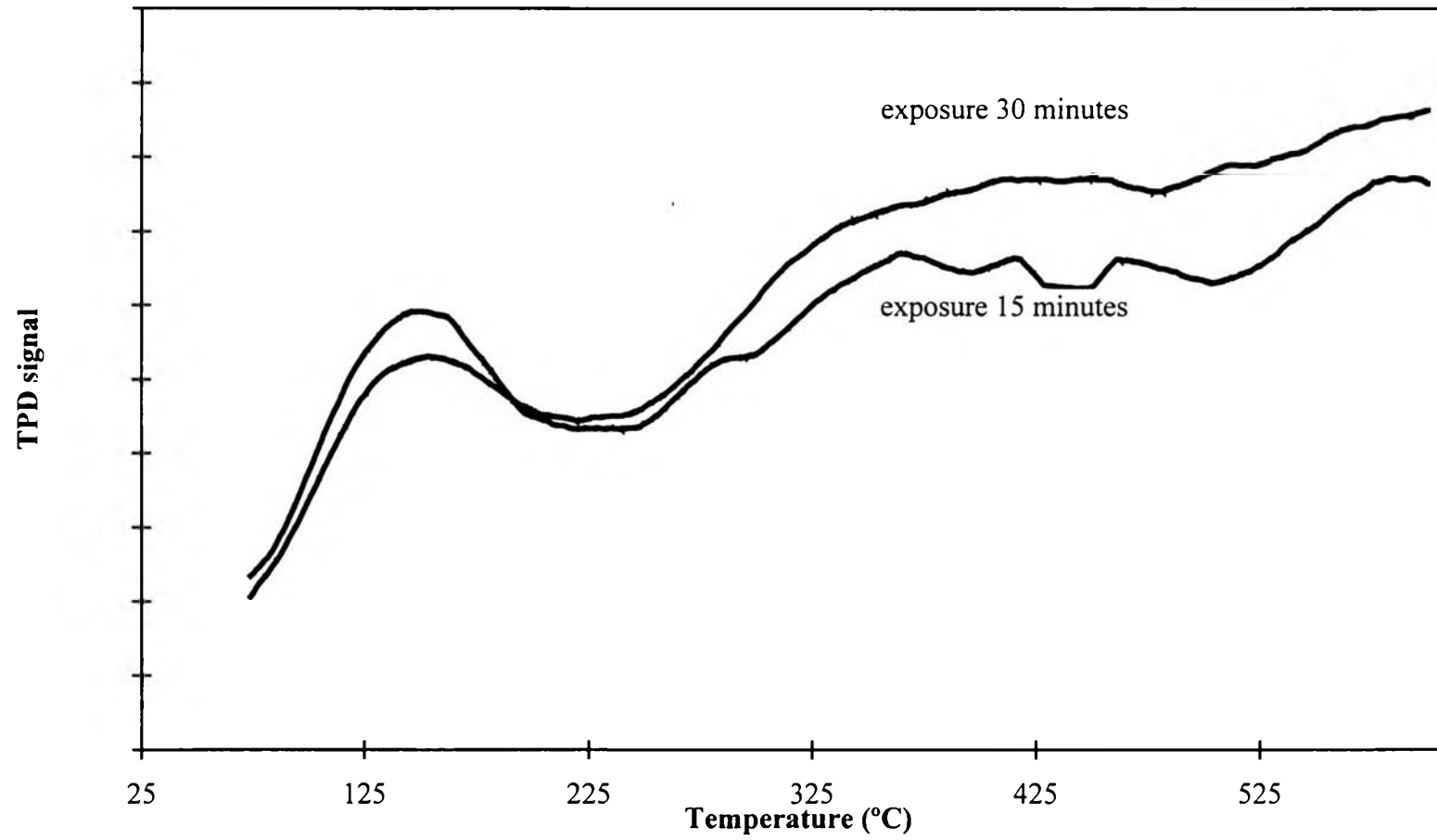


Figure 4.8 The temperature programmed desorption curve at 2 hours reduction time.

Figure 4.7 shows the effect of hydrogen reduction condition on TPD spectra. The adsorption of hydrogen on the Pd surface increases with the reduction time. Initially, the catalyst was in oxide form. Before starting the reaction, it should be reduced by hydrogen to change to metal form which is active form. So, when the longer time is used, more active forms will occur.

Figure 4.8 illustrates that at different exposure times, the TPD spectra show some differences in the first peak while the areas of the second peak are greatly changed. These two peaks are of two kinds of desorbed species, i.e., the surface hydrogen as the low temperature peak and subsurface and bulk hydrogen as the high temperature peak (Mavrikakis et al., 1996).

4.3 Catalyst Regeneration

Figure 4.9 shows the result of the catalyst regeneration. After fresh catalyst had been used in the reaction, the catalyst was regenerated at different temperatures and times. Regeneration at 200 °C could recover more activity than at 180 °C, since the regeneration was favored by high temperatures. The explanation for this might be the hydrogenation regeneration of the carbonaceous deposits on the metal surface as shown in Cortright et al. (1991)'s work using Pt catalyst. At high temperature, they found that carbonaceous deposit could be removed by reaction with hydrogen.

For the regeneration at 200 °C, the conversion is higher than its initial value. This might be due to the fact that in the initial reduction step, all of catalysts are not changed to active forms, as supported by the results shown in the TPD part. When hydrogen is passed for regeneration, the remaining oxide forms of catalyst will be changed to more active forms. Thus, these more active sites increase the conversion. For the regeneration at 300 °C, the conversion is lower than its initial value. Table 4.1 shows that pore volume

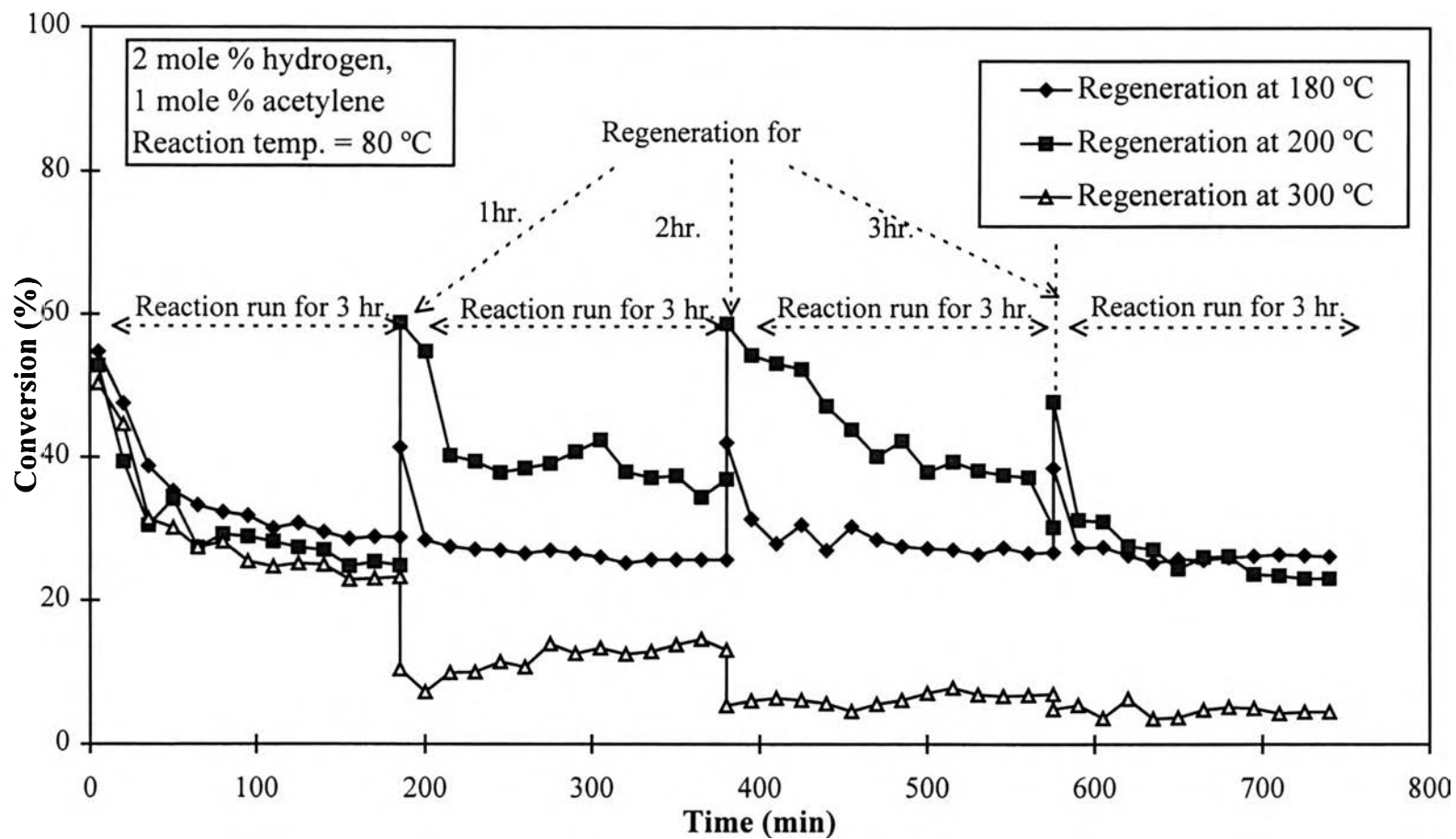


Figure 4.9 The conversion of acetylene for the cycle runs.

and pore radius decrease after regeneration at 200 and 300 °C. Regeneration at higher temperatures tends to result in decreasing pore sizes and pore volume.

Table 4.1 Volume-pore size summary by BET method

Catalyst	Pore Volume (ml/g)	Pore Radius (°A)
Fresh	0.01703	7.356
After regeneration at 200 °C	0.01366	6.365
After regeneration at 300 °C	0.01344	5.741

The decreasing pore size and pore volume would cause to lower the activity of catalyst. At every 185 minutes of operation, the catalyst was regenerated for 1, 2 and 3 hours, respectively. It was noted that the regeneration time did not affect the conversion. Although the regeneration time was increased, the activity of catalyst could not be more recovered.