CHAPTER I INTRODUCTION

1.1 General Knowledge

The hydrogenation of unsaturated hydrocarbons became of great interest in the sixties because of the booming growth of naphtha cracking for olefins. These nonselective thermal processes produced methane, ethane, propane and also a range of unsaturated hydrocarbons, such as acetylene and ethylene. This mixture had to be separated and purified to meet the specification of feedstock for down-stream petrochemical industry. In the manufacturing of polymer grade ethylene, the removal of acetylene, which presents as harmful contaminant in the C_2 rich cut obtained from cracking plants, is an important step. Generally, acetylene is present as approximately 1% in complex gas mixtures containing either approximately 10-20% of hydrogen (front-end mixtures) or essentially ethylene and ethane only (tail-end mixtures).

An elegant and widely used method is the catalytic hydrogenation of acetylene. With regard to the ethylene hydrogenation, the process must be highly selective since the acetylene content has to be reduced to less than 5 ppm, while higher ethylene losses are economically intolerable (Bos et al., 1993). Palladium based catalysts have been proven to be capable of meeting these demands.

The main reactions involved are

C_2H_2	+	H ₂	 C_2H_4	$\Delta H^{\circ}_{298 \text{ K}} = -172 \text{ MJ/kmole}$
C_2H_4	+	H ₂	 C_2H_6	$\Delta H^{\circ}_{298 \text{ K}} = -137 \text{ MJ/kmole}$
C_2H_2	+	2H ₂	 C ₂ H ₆	$\Delta H^{\circ}_{298 \text{ K}} = -309 \text{ MJ/kmole}$

The direct hydrogenation reaction from acetylene to ethane is so small that it is of minor importance (LeViness et al., 1984). In addition to these three main reactions, oligomerization may also occur, yielding a complex mixture of C_4^+ compounds, the liquid part of which is commonly called "green oil". In typical industrial processes a trace amount of carbon monoxide gas is added in order to obtain good selectivity towards selective hydrogenation of acetylene to ethylene.

In industrial practice, the selective hydrogenation of acetylene is usually carried out in adiabatic packed bed reactors. This reaction is accompanied by several chemical reaction engineering problems, in particular the phenomenon of thermal runaway, which is known to occur rather often in industrial practice. For a study of the stability and the dynamics of an adiabatic hydrogenation reactor, a thorough understanding of the kinetics involved in this reaction system is necessary.

1.2 Research Objective

This thesis project is a continuation of research work on selective hydrogenation of acetylene over Pd-Ag catalysts investigated previously by Pongbhai (1997). The objective was to develop a better understanding of interactions of hydrogen, acetylene and ethylene with a typical $Pd-Ag/Al_2O_3$ catalyst containing 0.03 wt % Pd loading and 0.235 wt % Ag.

The reaction of acetylene hydrogenation was studied in flow reactor experiments under differential conversions. The goal was to investigate the effect of hydrogen reduction condition on the temperature programmed desorption spectrum and to study the effect of acetylene concentration on deactivation of the catalyst. The effects of temperature and time on catalyst regeneration were also studied.