CHAPTER I INTRODUCTION

1.1 General knowledge

The hydrogenation of unsaturated hydrocarbons became of interest during World War II but the large scale industrial implementation of this process started in the sixties because of the booming growth of naphtha cracking for olefins. These nonselective thermal processes produced besides of methane, ethane, and propane also a range of unsaturated hydrocarbons, such as acetylene and ethylene. This mixture had to be separated and purified to meet the stringent specification of feed stock for petrochemistry.

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, the acetylene content in tail-end mixtures, i.e., the mixture of ethylene and ethane only, is approximately 1%. However, in order to meet the specification of a polyethylene plant's feed stream, the acetylene content must be reduced to less than 5 ppm. (Bos et. al., 1993). An effective and widely used method is the catalytic hydrogenation of acetylene to ethylene. This process must be highly selective and able to reduce the acetylene content to meet the polyethylene feed stream specification without causing the economically undesirable hydrogenation of ethylene to ethane. Palladium based catalyst have found to be capable of meeting this very stringent demand on hydrogenation selectivity.

The main reactions involved are

$$C_{2}H_{2} + H_{2} \rightarrow C_{2}H_{4} \qquad \Delta H_{298 K} = -172 \text{ MJ/kmole}$$

$$C_{2}H_{4} + H_{2} \rightarrow C_{2}H_{6} \qquad \Delta H_{298 K} = -137 \text{ MJ/kmole}$$

Recently, many studies, e.g., Margitfalvi et al. (1981), have found that the direct hydrogenation of acetylene to ethane is also involved in this process.

$$C_2H_2 + 2H_2 \rightarrow C_2H_6 \qquad \Delta H_{298 K} = -309 \text{ MJ/kmole}$$

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

The selective hydrogenation of acetylene, in industrial practice, is usually carried out in adiabatic packed bed reactors. From a reaction engineering standpoint, the process is very challenging. One of the problems is that the hydrogenation reactions are highly exothermic, so that thermal runaway reactions may occur. Carefully designed control strategies need to be employed to safely operate this process. A prerequisite for good control of steady state operation is a thorough understanding of the kinetics involved in this reaction system.

1.2 Reserch objective

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The objective of the thesis project is 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 kinetics of ethylene and acetylene hydrogenation are studied as a function of temperature and reactant partial pressures in flow reactor experiments under differential conversions. The goal is to establish power rate laws for the reactions and to determine apparent activation energies. The results of this thesis will provide important fundamental insight into the operation of selective hydrogenation catalysts, providing information that can be helpful in optimizing the actual industrial operation of such catalysts.