# CHAPTER I

# INTRODUCTION

Ethylene is the lightest olefin and is the basic chemical raw material for a large variety of industrial processes. The importance of ethylene for chemical industries results from the reactivity due to double bond in its molecular structure. Although ethylene is less reactive than acetylene, it is simpler, safer, and less costly to produce and further convert. As a result, ethylene has largely replaced acetylene as the basic building block for an entire branch of industrial organic chemistry. Ethylene does not freely occur in nature, but is generally produced by the pyrolysis or catalytic cracking of refinery gas, ethane, propane, butane and the like [Johnson M.M. *et al.*, 1984]. Ethane and natural gas liquids (often a mixture of ethane and propane) are preferably used in ethylene production. Produced ethylene contains small proportions acetylenic compounds, depending on feedstock used. An ethane feedstock produces the smallest amount of acetylene by-product, which averages about 0.26 wt% of the product stream. However, for other feeds, this quantity can become as large as 0.95 wt% [Larsson M. *et al.*, 1996].

The removal of acetylene contaminant in ethylene stream is vital, as acetylene acts as a poison to the catalyst used for polymerization of ethylene. Additionally, acetylene can form metal acetylides, which are explosive contaminants [Huang Y.-J. *et al.*, 1994]. Thus, less than 10 ppm acetylene and most preferably less than 5 ppm are allowed in polymergrade ethylene [Cosyns J. *et al.*, 1984].

One typical technique used for removing trace amount of acetylene in an ethylene stream has involved selective hydrogenation. Acetylene is catalytically hydrogenated. However, it is desirable that ethylene should remain intact during hydrogenation, since over-hydrogenation to ethane reduces yields.

Supported palladium catalysts have proved to be the best catalysts so far for the reaction with good activity for the hydrogenation of acetylene in excess ethylene. Numerous factors have been found to affect the selectivity of such palladium catalysts

[Cosyns J. *et al.*, 1984]. Typically, as the temperature is increased above that which gives substantial elimination of acetylene, there is a progressive increase in the amount of ethylene and acetylene that is converted to ethane. An increase in the amount of olefin that is hydrogenated results in runaway ethylene hydrogenation. It is thus desirable to be able to operate with the catalyst and condition that will allow a relatively wide spread between the temperatures with produces either effective elimination of acetylene or the small amount of ethane formation. Regrettably, oligomer or green oil formation during acetylene hydrogenation (which shortens the catalyst lifetime) and high ethylene loss due to ethane formation at high levels of acetylene conversion are still inevitable over palladium based catalyst [Boitiaux J.-P., *et al*, 1985].

Promotion with a second metal such as Ag [Huang D.C., *et al*, 1998, Zhang Q., *et al.*, 2000)], Au [Viscer C., *et al.*, 1974, Sárkány Á., *et al.*, 2002], Cu [LeViness S., *et al.*, 1984], Si [Shin E.W., *et al.*, 1998], K [Park Y.H., *et al.*, 1992], and Co [Sárkány Á., *et al.*, 1995] has been reported as an alternative way for selectivity enhancement for palladium catalysts. Among those bimetallic catalysts, Pd-Ag has been reported as a promising catalyst that can reduce green-oil formation as well as enhance selectivity.

The catalysts used for a long time will suffer activity loss from formation of green oil on its surface. To compensate for such activity loss, the operating temperature needs to be increased to maintain the conversion rate in a commercial plant. However, eventually the plant must be shut down, and the catalyst either regenerated to recover its activity or replaced with fresh catalyst. Regenerated Pd-Ag/Al$_2$O$_3$ catalysts usually show less activity and different selectivity compared with the fresh catalyst. [M.P. Kaminsky, *et al.*, 1994]

Moreover, pretreatment with nitrous oxide yields increased acetylene conversion and ethylene gain [Ngamsom B., 2002]. Pretreatment altered the catalyst morphology and bulk structure. Increasing in ethylene gain may result from blockage of palladium sites responsible for direct ethane formation via ethylidyne species. However, no research in pretreatment of nitrous oxide on used catalysts was reported.

In this study, fresh and spent commercial Pd-Ag/Al$_2$O$_3$ catalysts are used to model catalysts. Catalytic evaluation and characterization have been performed in order to clarify the effects of

## 1.1 Objective

This thesis is intended to given an understanding of effects regeneration on the properties of Pd-Ag catalysts for the selective hydrogenation of acetylene after N$_2$O activation.

## 1.2 Scope of this work

The study has been scoped as follows:

1. Preparation of 1wt%Pd-3wt%Ag/Al$_2$O$_3$ using the incipient wetness impregnation method.

2. Pretreatment of catalyst with N$_2$O by injecting certain amount of gas into catalyst prior to reaction test..

3. Catalyst evaluation as a function of time on stream.

4. Characterization of catalysts:

    - study of catalyst structure and morphology by X-ray diffraction (XRD)

    - study of metal dispersion by CO chemisorption

    - surface analysis by X-ray photoelectron spectroscopy (XPS), Fourier Transform-infrared spectroscopy (FT-IR) and Ethylene temperature program technique

    - measurement of carbonaceous deposits by temperature-programmed oxidation (TPO) and weight loss technique