# CHAPTER I

# INTRODUCTION

Metal supported catalysts are used to promote a variety of reactions involving hydrocarbon feedstocks. The synthesis of propylene by dehydrogenation of propane is a reaction that the catalysts play an important role in decreasing reaction temperature and increasing product selectivity. The thermodynamics of the dehydrogenation reaction are such that it is desirable to work at high temperatures and low pressures, but these are the conditions that favor the formation of carbon compounds, commonly called coke, on the catalyst surface, which results in catalyst deactivation. The deactivation which causes changes in activity, selectivity and stability of the catalysts is an important problem, especially in the case of large scale production.

According to some workers, coke may be considered to be formed by two fractions (Pieck 1989), one of which is deposited on the metal and the other on the acidic support. However, only burn-off of the coke on metallic sites is necessary for propane dehydrogenation because activity depends on a great extent of metallic sites.

Coke deposition is a complex reaction that results from the production of coke precursors and from their destruction (Barbier 1986). It is reported that there are two major types of carbon structure; the largest part consisting of pseudographitic carbon and the rest poorly organized polynuclear aromatic systems (Tanabe 1989). The mechanism of coke formation is complex with multi-step reaction sequences and greatly differs by catalyst-reactant system used. Dehydrogenation, isomerization (condensation), hydrogen transfer, cyclization and aromatization are the reaction generally involved (Tanabe 1989). Coke formation is related to the acid-base properties of the catalyst-reactant system. It has been indicated by several investigators that strong acids rather than weak acids, Lewis acids rather than Brϕnsted acids favor coke formation (Tanabe 1989). It is obviously clear that there are several pairs of $\pi$ electron upon carbon structure and it exhibits the basicity of coke. Thus, the acidic sites rather than the metallic sites favor coke formation as Lesis acids.

The formation of the carbon deposits, requires several metallic sites, blocks the metal and plugs the support porosity leading to catalyst inactivity. However, the remedies for deactivation can be derived from an understanding of the mechanism of coke formation and of its effect on the activity and selectivity of the catalysts.

It is now a well known fact that for the $Pt/Al_2O_3$ type catalysts, carbon deposition can be considerably inhibited by the addition of a second component such as Sn. The major role of the second component of platinum-containing bimetallic catalysts is the enhancement of the stability of such catalysts under severe reaction conditions (Tao 1994, Liwu 1990, Yining 1991) and may preserve activity by poisoning the more acidic sites in the alumina support (Beltramini 1987). The effect of Sn as a promoter depends on the support. On $\gamma$-$Al_2O_3$ tin interacts with the support and is stabilized in an oxidation state greater than zero. The result is an increase in Pt dispersion and reduced deactivation without any change in the initial specific activity in dehydrogenation (Barias 1995).

A previous work (Somsak 1992), which studied the activity of dehydrogenation catalysts, has pointed out that from the first 40 minutes of the coking reaction, conversion of propane is rapidly dropped and then shows no further major change with the time of reaction, while the conversion is very low, surprisingly being always more than zero. It is explained that some metallic sites are still exist after operation. On the other hand it has been proved that an amount of coke increases with the time on stream. These evidences suggest that the increasing amount of coke accumulated on the support. Coke cannot cover the whole metallic sites due to the requirement of several metallic sites, or too small metallic sites exist.

Coke on dehydrogenation catalysts can be classified into two major types using combustion temperature which are reversible (partially hydrogenated) and irreversible (graphitic) coke. The first one can be easily removed by hydrogen while the latter is less readily (Biswas 1987). Both types of coke are similarily deposited on the acidic and metallic sites.

The Temperature-Programmed Oxidation technique is commonly used in characterization of coked catalyst to give information of the total amount of carbon by measuring the amounts of carbondioxide produced. The results obtained from temperature-programmed oxidation of coke in the temperature range of 0-700°C indicated three oxidation zone as showed in figure1.1 (Atchara 1995); the first peak located at about 110°C. The second was at about 450°C and the last was at about 500°C. The kinetic parameters (Ea/R) of coked combustion were approximated by Atchara (1995) that the values of the coke on the metal sites (coke 2) was 11100 K and that of coke on the support (coke 3) was about 4560 K. Good agreement was obtained between the simulation results and the experimental results. The data, however, did not expressed clearly the detail of mechnism on coked combustion.

This work is intended to characterize the coke deposits on a propane dehydrogenation catalyst by temperature-programmed oxidation and BET surface area measurement techniques. The role of metal during the combustion process is also an study subject in this research. In addition, the effect of reaction time on coke structure is also investigated.

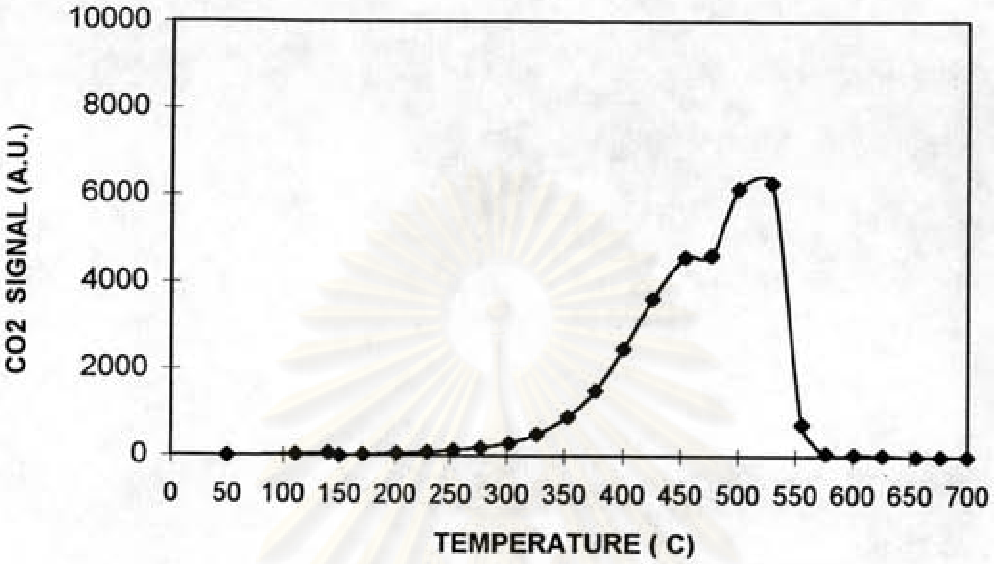

Figure 1.1 TPO spectrum of coked Pt/Al2O3 catalyst from 600°C propane dehydrogenation, $H_2$/HC =0, reaction time = 40 min. (Atchara, 1995)

The present work is arranged as follows, chapter II presents a literature review of investigation on coked catalysts.

The theory of this work, studies overview of deactivation by coking, effect of carbon deposits on the dehydrogenation reaction, composition, structure and localization of coke, coke formation kinetics , BET method and pore size distribution are presented in chapter III.

In chapter IV, the experimental systems and the operational procedure are described.

The experimental results obtained from a laboratory scale reactor and standard measurement are reported and discussed in chapter V.

Chapter VI gives overall conclusion emerged from this work and presents some recommendations for any future works.

Finally, $CO_2$ calibration curve for gas chromatography, calculation of external and internal diffusional limitations on both dehydrogeanation and coke combustion reaction, some information of Pt-Sn/$Al_2O_3$ catalyst, data of TPO results, and data of pore size distribution are included in appendix at the end of this thesis.