CHAPTER I

INTRODUCTION

In the early years of the 19th century, a majority of industries have used catalysts in order to decrease time and temperature of reaction and increase selectivity of product. The catalyst may lose its activity in the causes of poisoning, fouling, loss of active site and loss of active species. The deactivation of catalysts by coke deposit is an important problem in petrochemical industries, both from an economics and technological. The loss of catalyst activity due to the accumulation of coke makes it necessary either to stop the unit to regenerate the catalyst or to adapt different technologies such as alternately swinging out a reactor from the reactor train for regeneration or with continuous regeneration of the catalyst moving from reaction to regeneration zone.

Coking is a common deactivation mode in hydrocarbon conversion processes which is formed and deposited on the surface of catalyst. It is a mixture of mono- and polycyclic aromatic rings connected by aliphatic and alicyclic fragments.

Coke deposition is a complex reaction that results from the production of coke precursors and from their destruction [1]. 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 [2]. 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 [2]. 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 Bronsted acids favor coke formation [2]. It is obviously clear that there are several pairs of electron upon carbon structure and it

exhibits the basicity of coke. Thus, the acidic sites rather than the metallic sites favor coke formation as Lewis acids.

The formation of the carbon deposits, requires serveral 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.

Several techniques have been used to study the carbonaceous residues, eg, Fourier Transform Infrared Spectroscopy (FTIR) [3,4], Transmission Electron Microscope (TEM)[5-7], Laser Raman Spectroscopy (LRM)[8], Electron Energy-Loss Spectroscope (EELS)[9], Carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR) [10], Auger Electro Spectroscopy (AES) and Secondary Ion Mass Spectrometry (SIMS) [11], Small-Angle Neutron Scattering (SANS) [12], Temperature Programmed Oxidation (TPO)[13-21], etc. All these techniques give different types of information on coke composition, structure and location. The most widely used technique to characterize coke deposite is the temperature programmed technique. It has been used to characterize coke in several catalytic system, such as reforming catlysts[13-18], zeolites[19], Ni catalysts[20,21], etc.

The temperature programmed oxidation technique is used to give information of the total amount of carbon by measuring the amount of carbondioxide produced. TPO curve of coked catalysts shows two peaks, one at around 300 °C could be coke deposite on metal site and the other coke on alumina support at 450 °C. Measuring the oxygen consumed and carbon dioxide produced corresponds to the formula CH_x [22].

Dehydrogenation is a reaction in which hydrogen is eliminated from a molecule. Dehydrogenation of alkane is one at the most important reaction to increase chemical feedstocks. The thermodynamics of the dehydrogenation reaction are such that it is desirable to work at high temperature and low pressure but these are the

conditions that favour coke formation. Therefore, there are many studies trying to improve the performance of the present catalyst and to develop new catalysts that give the desired results.

A typical catalyst used in dehydrogenation process is Pt/Al_2O_3, which is known having a short catalyst life time. Additives such as Re, Ir reduce coke formation and result in longer catalyst life[2,22]. Beltramini and Trimm[23] compared Pt, Pt-Re, Pt-Ir, Pt-Sn and $Pt-Ga/Al_2O_3$ catalyst and found that bimetallic catalysts could control activity, selectivity and coking better than the monometallic catalyst.

The addition of tin has proved to be an effective way to enhance the propane selectivity and prevent deactivation due to coke formation. Tin promotes the catalyst by increasing platinum dispersion and reduces the strength of chemisorption of hydrocarbons on metal surface. Thus, carbon precursor could migrate towards the support easier[24-25].

Alkaline and alkaline-earth metals are the third metal added to bimetallic catalyst to reduce acidity of catalyst, therefore reduces coke on acidic support. Chen and Char[26] revealed that the addition of alkali and alkaline-earth metals improved resistivity to coke formation and sintering on Ni/Al_2O_3 catalyst. Alkali can act as textural promoter so it can reduce coke on metal active sites more than $Pt-Sn/Al_2O_3$ catalyst [27,28]. The study of additional potassium on $Pt-Sn/Al_2O_3$ showed that it could decrease the amount of low temperature coke on metal active sites. It may due to potassium might increase hydrogen spillover to remove coke precusor [29].

From the above mention, $Pt-Sn-K/Al_2O_3$ catalyst is a proper for degydrogenation reaction. In addition, reaction conditions such as temperature, pressure, reactants, etc. also have some effects on coke formation. In real operating process, there are also several factors involving raw material which depend on source of raw material and economic.

The aim of this thesis is to get a better understanding of coke formation during alkanes and alkenes dehydrogenation. As a matter of fact, alkenes are main product in dehydrogenation of alkanes. Thus,this study was selected some alkenes as reactants to study factors that effects of coke formation also. The coke catalysts after dehydrogenation were characterized by TPO technique.

The present research work is organized as follows:

Chapter II presents a literature review of investigation on coked catalysts.

The theory of this research, studies overview of deactivation by coking, effect of carbon deposits on dehydrogenation reaction, composition, structure and localization of coke 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 conclusions emerged from this work and presents some recommendations for any future works.

Finally, calculation of temperature in saturator, calculation of catalyst praparation, calibration curve of carbon dioxide content, specification of alumina support (Al_2O_3) type KNH-3 from Sumitono Aluminium Smelting CO.,LTD, and temperature programmed oxidation curve are included in appendix at the end of this thesis.