CHAPTER I

INTRODUCTION

In most heterogeneous catalytic processing of hydrocarbons (petroleum refining and petrochemical industries),a carbonaceous deposit called coke is usually formed on the catalyst surface. Coke formation is an unavoidable side reaction which can be formed by reactants (parallel deactivation), by products (series deactivation), or by both. However, this phenomenon is unlike other causes of catalyst deactivation such as irreversible poisoning or sintering, the deactivation caused by catalyst coking is reversible; coke deposit can be eliminated by burning.

It is accepted that coke is made up of polyring compounds and that the number of rings in these compounds increases as a function of time in operation. The polyring compounds produce a turbostratic structure which after a long period of operation could lead to a graphite structure. The turbostratic structure was described as a model of disordered carbons, these materials consist of nearly perfect graphite layers arranged in parallel stacks, but with little interaction between adjacent layers [1].

The knowledge in the field of coke deposition have been studied in several aspects which concern in the structure of the carbonaceous species formed on a catalyst, their relationship to the feed composition, and also the operating conditions. Extremely various and complex reactions should be involved in the process of coke formation Therefore, it makes difficulties to study the mechanism by which deactivation occurs.

Coke deposit on catalysts are commonly categorized by burning temperature. The thermal techniques such as thermogravimetric analysis (TGA) and temperature programmed oxidation (TPO) can provide the burning temperature and total amount of coke deposit. Nevertheless, the information of coke structure is not given by these techniques. Moreover, the conclusion of

whether different burning temperature caused by different coke structure or coke location (on metal site or support) is still subject to some disputations.

Infrared spectroscopy technique (IR) is used extensively in obtaining detailed information on the molecular structure of various organic and inorganic compounds. The application of infrared spectroscopy has now become important in catalysis study. This technique has been employed in characterization of catalyst surface structure and composition, adsorbate structure and adsorbed species formed under reaction conditions [2-4].

The system of coke deposit on a catalyst composes of two main compounds in which coke is an organic compound adsorbed on inorganic compound of catalyst. From a theoretical point of view, the analysis of coke deposit on this system seems to be possible by using infrared spectroscopy technique. In fact, it still has complexity in practical from several reasons. First, the coke itself is inherent dark color compound, this makes it almost completely absorb infrared radiation and leads to unwell resolved of infrared spectrum. The second problem is produced by oxide surface of support. γ-Al_2O_3 is the most popular oxide support used in dehydrogenation catalyst. Although it has great properties for being support of catalyst, the alumina surface is complicated and difficult to deal with experimentally. The surface of alumina is mostly covered by adsorbed water that can retain in alumina structure even though at high temperature, i.e. higher than $500^{o}C$. Furthermore, at ambient temperature a significant amount of CO_2 can adsorb on alumina surface [5-7]. The adsorbed species from water and CO_2 originate several infrared adsorption bands which disturb or hinder absorption bands of interested surface species.

Accordingly, characterization the structure of coke deposit on catalyst surface by application infrared spectroscopy is interesting. This technique still need to be developed so as to suppress these difficulties. This research suggests the development of infrared spectroscopy technique to study molecular structure of coke deposits on a dehydrogenation catalyst. It is the subject of the present

work to demonstrate and discuss factors effect the infrared characterization of deposited coke. In this experiment, the coked catalyst was prepared in lab-scaled dehydrogenation reactor apart from infrared spectroscometer prior to examine by in-situ IR. The results received from this research can lead to the possibility in studying of coke formation simultaneous with the progression of reaction which will be analyzed by in-situ IR.

This research 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 , and the theoretical consideration on infrared spectroscopy technique are given in chapter III.

Follow by description of the experimental systems and the operational procedures in chapter IV.

The results obtained from infrared characterization are reported and discussed in chapter V.

Chapter VI conducts to the overall conclusion emerged from this study and delivers some recommendations for any future works.

Finally, infrared spectra of coked catalyst at sample temperature 300°C, 400°C, and after cooling down to room temperature in N_2 atmosphere including a briefly information about Fourier transform infrared spectroscometer (FT-IR) are collected in appendices at the end of this thesis.