



CHAPTER I INTRODUCTION

Catalytic reforming has become one of the most important industrial applications of catalysis. In this process, saturated hydrocarbons (alkanes and cycloalkanes) in petroleum naphtha fractions are converted extensively to aromatic and other hydrocarbons which have a much higher anti-knock quality as automotive fuels; the aromatic/hydrocarbons are also used as feedstock for petrochemical industry. Paraffins, which are the main components, produce the desired reaction of dehydrocyclization. Additionally, other reactions involving dehydrogenation, cyclization and hydrogenolysis are also led to the formation of aromatic hydrocarbons. Among these paraffins, the five or six carbons produces the most important coke precursor [1].

Operating conditions for the process reflect the balance between the thermodynamics of desired and undesired reactions. Desired reactions are favored by high temperatures and low pressures, conditions that also favor coke formation [2-6]. Deposition of coke (coking) is one of the four basic deactivation processes and its main effect is the physical blocking of the catalyst surface (including its pores), which is called "fouling". However, it has been reported that coke may have some poisoning effect on metallic and acid sites. The forms of carbon deposition (usually called "coke") may vary from high molecular weight hydrocarbon species (polymeric carbon) to graphitized carbon corresponded to the formula CH_x [1,7-13]. There is general agreement that this envisions coke formation as more of a polymerization process than a degradation process [2, 14-19]. Overall, such results and interpretation suggest that coke precursors are the simpler feed molecules and that fragments, via polymerization or dehydrogenation reactions, form larger polynuclear aromatic intermediates characteristic of structures found by x-ray examination of coke.

Furthermore, analysis by temperature programmed oxidation (TPO) generally indicated two types of coke: the first one burns at low temperatures (polymeric carbon), which is associated with the metallic phase. The second type burns at high

temperatures (amorphous phases/graphitized carbon), corresponded to the support [3, 4, 13, 20-23].

Generally, the standard reforming catalysts are Pt-based catalysts (especially Pt/Al₂O₃) [7, 24-33]. It has been found possible to use multimetallic catalysts supported on alumina to promote reforming. Combinations of Pt-Re, Pt-Ir, Pt-Sn and Pt-Ge have been reported and are now used widely in industries. The essential contribution of such catalysts has greater stability.

The major difficulty in the determination of modes of coking and of deactivation is to establish the composition of coke. In situ spectroscopic methods (IR, ¹³C-NMR, UV-VIS, EPR) can give information concerning the coke content, the chemical identity of coke components during the reaction, the nature of active sites and the modes of deactivation [34-46]. Unfortunately none of these methods is able to give the coke composition. Consequently, to determine the complete distribution of coke components, various techniques have been used to recover the compounds trapped in the catalyst pores. The direct treatment of coked catalyst by an organic solvent or under an inert gas flow at high temperature allows the recovery of a small part of carbonaceous compounds [47-51]. Soluble coke components can be extracted with an organic solvent. The internal coke compounds can be liberated by solubilizing the catalyst in acid solutions. The soluble coke components were analyzed by classical methods such as gas chromatography (GC), high-performance liquid chromatography (HPLC), ¹H NMR, IR, mass spectrometry (MS) etc. In this case the distribution of these components (and not only their nature) was obtained. The non-soluble coke was characterized chemically (atomic hydrogen-to carbon ratio) employing Temperature Programmed Oxidation (TPO), and physically using electron microscopy, electron energy loss spectroscopy.

The literature reviews focused on: kinetics of coke deposition; influence of bimetallics; effect on different metal active sites and structure of coke [52-67]. However, the coke growth on the metal and the support site has not been investigated sufficiently so far. That the rate-determining step of coke formation is polymerization

is the criteria. Like the coking mechanism, the Fisher-Tropsch reaction (FT) is also the polymerization with the addition of carbon intermediates. Recently, the chain growth of FT synthesis product is calculated from the Schulz-Flory distribution theory. Accordingly, it can be applied Schulz-Flory distribution theory to calculate these values (usually called alpha value), the relationship between carbon atoms and weight fraction or hydrocarbon distribution. Coked catalyst must be recovered by a Soxhelt extraction and then analyzed through adequate techniques (GC/MS, HPLC, etc.)

In light of these considerations, it is important to know which of the two functions, metal or acid (alumina), controls the deactivation behavior of the reforming catalysts. In order to shed some light on this matter, the physically mixed Pt/SiO₂ and γ -Al₂O₃ was used in this work as a representative catalyst of Pt/Al₂O₃. The appropriate size of Pt/SiO₂ mixed with Al₂O₃ gave the same behavior, such as catalytic conversion, active site, H₂ spillover, acidity, coking etc., that obtained from the conventional Pt/Al₂O₃ catalyst. Since the SiO₂ support in Pt/SiO₂ has a very low acidity, its contribution to the acid function is, therefore, negligible [68-70].

Thus, the subject of this work is the study of coke formation on the metal and the support site employed a physically mixed system (Pt/SiO₂ represented the metallic site and Al₂O₃ represented the support site) under various parameters such as time, temperature, H₂/HC ratio and the type of catalyst. The main goal was to determine the probability of chain growth of coke formation on both sites using the Schulz-Flory distribution in order to understand the deactivation process of catalyst.

The scopes of this study have to be taken into account.

1. Prepare Pt, Pt-Sn and Pt-Sn-K catalyst by using the dry impregnation method.
2. Study the combination of platinum and alumina for study catalyst deactivation.
3. Coking reaction test using the hexane dehydrogenation with various conditions.

4. Removal of carbonaceous deposits by a Soxhlet extraction with toluene solvent.

5. Characterization of fresh and coked catalysts by the following methods.

- active site by CO adsorption
- chemical identity by IR
- surface area by BET
- amount of coke by TPO
- graphitic phase of coke by XRD
- morphology modification by TEM
- carbon radicals of coke by ESR
- nature of soluble coke by GC/MS and GC-14B (a DB 1 capillary column)

The present research work is divided into 6 chapters. To accommodate a variety of backgrounds of readers, it begins with introduction that is necessary for the understanding of deactivation process called coking in chapter I. Chapter II is concerned with a literature review of investigation on coked catalyst. In chapter III, it provides readers with a detailed overview of theory of reaction by coking, effect of carbon depositions on dehydrogenation, composition and structure involving the Schulz-Flory distribution applied for calculating the probability of chain growth of coke formation. A comprehensive examination of the coking processes consisting the experimental system, the operation procedure and the characterization method are presented in chapter IV. Next, chapter V demonstrated the experimental results obtained from a laboratory scale reactor, standard measurement including an expanded discussion. The conclusion is given chapter VI. This reorganization contributes to a better understanding of all of the critical aspects of coking deactivation process. At the end of this research, appendices contain calculation of catalyst preparation, an overview of calculation of temperature in saturator, calculation of active site, calibration curve of carbon dioxide content, calculation of probability of chain growth and specification of alumina support (Al_2O_3) type KNH-3 are summarized.