สำนักงานวิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I

INTRODUCTION

In any hydrocarbon processing, coke deposition leading to catalyst deactivation is seemingly unavoidable. Therefore, a considerable effort has been focused on the characterization of carbonaceous deposits. Different was used to obtain information about the location, composition, and structure of coke deposits, e.g., TEM, Laser Raman Spectroscopy, EELS, and ^{13}C NMR . However, the most widely technique is temperature programmed oxidation (TPO). This technique has been used to study coke on naphtha reforming catalysts, zeolites, Ni catalysts, etc. Currently, TPO is performed with the following detection methods:

-determination of CO_2 by a thermal conductivity detector (TCD) after it is separated from oxygen in a GC column;

-quantification of CO_2 with a mass spectrometer;

-monitoring temperature increment above a reference sample, in differential thermal analysis (DTA) equipment;

-measurement of weight loss in thermal gravimetric analysis (TGA) equipment

The detection of CO_2 using a TCD requires the separation of CO_2 from O_2 via a GC column and, therefore, is a continuous analysis. This analysis misses the fine structure, peak height, and peak temperature. The use of a mass spectrometer makes it possible to sample in intervals of a few seconds, but it is not as simple as TCD. During differential thermal analysis, metal, sulphur, and contaminants contribute to the signal. Additionally, it is very difficult to determine kinetic parameters. In thermal gravimetric analysis, plug flow through the sample is often not possible and thus the coke oxidation kinetics are greatly influence by oxygen oxidation. Also this technique has limited sensitivity and the weight loss does not always result from burning off coke deposits: interference from metal oxides formation, dehydroxylation of the support, and sulphur oxidation

In this paper we describe a new detection method which is simple and highly sensitive for TPO of coke deposits. The unit consist of a Model AMI-1

temperature programmed apparatus, manufactured by Altamira Instruments, Inc., and a computer-controlled valving system for the selection of the desired gas stream among many to the sample cell. Without modifications, the AMI-1 apparatus is not suitable for analysis of coke deposits since it has only a TCD and is without a GC column. The new detection scheme involves the conversion of CO_2, a flame ionization detector (FID) insensitive gas, to an FID sensitive gas, CH_4, in the presence of an oxygen-containing carrier gas. This is achieved by the addition of a small reactor, filled with a Ru catalyst, and places after the sample cell. When hydrogen is added to the reactor, the Ru catalyst hydrogenates CO_2 to CH_4 quantitatively. The CH_4 generation rate is continuously monitored by an FID. A GC column is not needed, FID is not sensitive to O_2 and H_2O present in the gas stream coming from sample cell.

Group VIII metals have been used for the hydrogenation of CO_2 to CH_4. Ruthenium and rhodium were found to have the highest activities and selectivities for the reaction (21). All the above studies were performed without a continuous flow of oxygen to the methanation catalyst. In TPO of coke deposits, the gas coming from the sample cell contains oxygen, since excess oxygen is required in the TPO experiments. Therefore, it is necessary to study the influence of oxygen in the hydrogenation of CO_2 to CH_4 and to establish the optimum condition for TPO experiments in connection with the new detection method. The improvements in sensitivity and spectrum resolution obtained by the new detection method are demonstrated when they are compared with spectra obtained by a TCD (via a GC column), TGA, and DTA.

1.1 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation is a method for coke characterization. The coke characteristic such as reactivity and behavior of coke regarding the thermal treatments can be obtained. Interpretation of this technique contributed to some information for catalyst regeneration.

In TPO technique, first spent catalyst is gradually heated so its temperature increases linearly with time, generally the O_2 in inert gas such as He is continuously

passed to the sample. Once the temperature reaches to the oxidizing temperature, the coke on the catalyst is oxidized by O_2. This can be explained by oxidation reaction (Querini and Fung, 1994).

$$CH_h + (1+h/4)\ O_2 \longrightarrow CO_2 + h/2\ H_2O \qquad (1.1)$$

Products of this oxidation typically are H_2O, CO_2 and also CO if the combustion (oxidation) is incomplete. CO_2 can be detected by Thermal Conductivity Detector (TCD) or mass spectrometer. Another option for better CO_2 detection is that the product gases are passed to methanator in order to convert CO_2 to CH_4.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad (1.2)$$

Then, Flame Ionization Detector (FID) is used to detect CH_4, which will give better results because FID has lower detection limit to CH_4 than CO and CO_2 detection limit of TCD.

1.2 Coke Formation

Carbonaceous deposit on catalysts occurs in a reducing environment, such as acid catalysts (non-metallic). On nonmetallic catalysts the deposit may contain considerable hydrogen, represented by an empirical formula CH_x in which x vary between about 0.5 and 1. Carbon depositions on metallic catalyst contain little or no hydrogen.

Many reactions can cause carbon deposit for example the disproportionation of CO ($2CO \longrightarrow C + CO_2$), the decomposition of CH_4 ($CH_4 \longrightarrow C + 2H_2$) and other gaseous reaction ($2H_2 + CO_2 \longrightarrow C + 2H_2O$) (Satterfield, 1991).

In thermodynamic equilibrium conditions, for the composition-temperature zone which in difference surface of catalyst results in temperature is different (solid carbon is thermodynamically stable), the graphite occurrence is more than dent carbon or active form of carbon. Moreover outside the composition-temperature zone, coke also occurs. The reason for this is that the carbon forming reaction are inherently faster than the carbon-removal reactions.

Typically, in metallic catalyst, carbon is formed as filaments "filamentous carbon". Filamentous carbon have the head of the growing filament contains a small crystal or particle of metal (or metal carbide) of about the same diameter as the filament, typically less than 0.5 μm.

Advantage of filamentous carbon.

In advantage of filamentous carbon, the disintegration of head as the filament grows and the disintegration of filaments causes a finely divided carbon containing some metal. The finely divided carbon may become catalytically active. By another hand in disadvantage of filamentous carbon when the time increases, the fibrous carbon structure may sinter and become more compact, resulting in catalyst deactivation.