

CHAPTER II

LITERATURE REVIEWS

Deactivation, due to coke formation, is a complex process. There are many works in the literature dealing with the chemistry and kinetics of catalyst deactivation by carbon deposition, but there are not many relating to the structure of carbon deposits. Information can be obtained with various spectroscopic techniques and even with diffraction techniques when the coke is graphitized. Analytical techniques such as chemical and chromatographic analyses of extracted coke and temperature-programmed oxidation (TPO) are also helpful. Researchers have sought to determine the structure of coke deposits, which will bring about a better understanding of its nature.

2.1 Reviewed Papers

In this section, special attention of related papers devoted directly to the analysis of coke deposition using infrared spectroscopic technique. However, the others points which related to other techniques are also mentioned so that all information can contribute and lead to some interesting subjects concerned in this thesis.

Eberly et al.[8] studied the structure of coke deposited on silica-alumina cracking catalyst by infrared technique. The coked catalysts were prepared from catalytic cracking of various hydrocarbon feeds in order to study the effect of different types of feeds to the structure of coke deposit. The coke deposit was isolated from the catalyst and pressed into a glassy pellet with KBr matrix for IR examination. The IR spectrum of fresh silica-alumina catalyst represented a broad absorption band centering around 3500 cm^{-1} which was due to stretch vibration in hydrogen-bonded OH groups on the fresh catalyst surface and in the adsorbed water. A strong band also appeared at 1640 cm^{-1} which was due to a hydrogen-oxygen vibration in the adsorbed water. The strong IR absorption bands below 1200 cm^{-1} were due to Si-O (1170 cm^{-1}) and Al-O (1080 cm^{-1})

linkages. For the IR spectrum of coked catalyst, aromatic C-H absorption was observed at 3050 cm^{-1} , methylene groups were seen at 2930 and 2860 cm^{-1} . A relatively intense band at 1580 to 1590 cm^{-1} indicated the characteristic of aromatic skeletal vibration. The aromatic bands were fairly strong in comparison with the combined intensities in the C-H stretch region (2800 - 3100 cm^{-1}). From this evidence, this paper pointed out that the coke deposit must be low in hydrogen content, indicating a high degree of condensation toward a pseudographitic structure. They determined the relative aromaticity of coke by estimation from the ratio of absorbance at 3050 cm^{-1} to absorbance at 2930 cm^{-1} . The result of relative aromaticity depended to some extent on the hydrocarbon obtained from various hydrocarbon feeds used in this paper. The coke obtained from cracking C_{16} normal hydrocarbon was decided to have more paraffinic than those obtained from aromatic feeds.

The infrared spectra of carbon deposited on $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Pt-Re}/\text{Al}_2\text{O}_3$ catalysts from the experiment of Ludlum and Eischens [9] were obtained under in-situ decomposition of acetylene. Their significant aspects of the assignment related to the carbon-oxygen bonds. The bands of the 1570 and 1450 cm^{-1} were observed from coked catalyst sample of $1.3\text{ wt.}\%$ carbon. These bands were attributed to the asymmetric and symmetric carbon-oxygen stretching vibrations of the carboxylate groups. However, coke was expected to have an aromatic content and the carbon-carbon stretching vibrations of aromatic rings also produced bands in the 1600 - 1400 cm^{-1} region. Formation of carboxylate from hydrocarbon showed that oxygen was provided by alumina, and they proved that formation of carboxylate was attributed to a hydrolysis reaction involving surface hydroxyl.

Lange et al.[10], using infrared and ^{13}C -NMR studies, provided evidence for successive steps in coke formation upon reaction of ethene over the zeolite hydrogen mordenite. The discussion here emphasizes only on infrared analysis. The spectra were obtained by in-situ IR system under non-isothermal conditions. At room temperature, ethene polymerized giving raised to

paraffinic IR bands which appeared between 2800 and 3000 cm^{-1} and between 1350 and 1470 cm^{-1} . The presence of branch alkanes were evidenced by the doublet at 1368 and 1382 cm^{-1} , ascribable to a deformation mode of isopropyl or tert. butyl CH_3 groups. Above 500 K, the high-temperature coke; which Lange et al. examined in their past work and defined as highly unsaturated radical species that was characteristic of carbonaceous matter, began to form, evidenced by an increase of the so-called coke band around 1600 cm^{-1} and a decrease of the paraffinic band between 2800 and 3000 cm^{-1} . The coke band might be indicative of polyalkenes and/or aromatics. Upon further increased of the reaction temperature, the coke band intensified and a band appeared around 1540 cm^{-1} . This band was ascribed to alkyl naphthalenes. However, it might also indicate polyphenylene structures. At 427°C, only traces of alkanes were detected. The observation was similar under isothermal condition. During an on-stream deposition of coke at 300°C on the same catalyst, an occurrence of paraffinic CH deformation bands could be observed between 1350 and 1500 cm^{-1} . Only after some 20 to 30 minutes delay did the IR bands of high-temperature coke appear, first at 1600 cm^{-1} and subsequently around 1540 cm^{-1} .

Among the coke characterized techniques, the temperature-programmed oxidation is commonly used, and has led to the results on the location of coke on reforming catalyst. However, the question of how far from a given particle the coke built up, and also the structure of these coke deposits were not well established as yet. For that reason, Gallezot et al. [11] studied the location and structure of carbonaceous deposits formed on a Pt/ Al_2O_3 catalyst on a microscopic or nanoscopic scale coked with cyclopentane for 4 hours by transmission electron microscopy (TEM) and by electron energy loss spectroscopy (EELS) associated with high resolution scanning transmission electron microscopy. The TEM investigation showed patches of amorphous coke covering the support surrounding each metal particle. The EELS was substantiated showing that the coke coverage could extend as far as 20 nm. from a given particle. From a comparison of EELS peak with reference compounds (graphite,

coronene, and pentacene), it was concluded that the local structure of coke was not graphitic or pregraphitic but might consist in a disordered arrangement of polyaromatic molecules.

The coke remaining after partial burning of coke deposits during the commercial Pt-Re/Al₂O₃ catalyst obtained from a commercial reforming operation with accumulated carbon 12.2 wt.% from 6 months of operation were studied by Pieck et al [12]. Burning temperatures were 350°C to 650°C, and the partial burning coke catalysts were concentrated by acid elimination of the support and investigated by infrared. The IR spectra of coke samples; pressed into disk with KBr, were showed in range 1000-1800 cm⁻¹. The absorption band appearing between 1480 and 1680 cm⁻¹ in original coke as well as partially burnt sample could be ascribed to the stretching of the C=C bond belonging to olefins, aromatic rings, and polyaromatics. The peak at about 1400 cm⁻¹ could be ascribed to the CH bond bending in CH-(CH₃)₂ or C-(CH₃)₃ groups. The absorption peak at about 1200 cm⁻¹ was due to the stretching of the CH group in the aromatic plane. The partially burnt sample presented an absorption peak approximately at 1715 cm⁻¹ due to the group C=O and another peak at 1100 cm⁻¹ which could be due to C-OH, because a broad peak in the range 3400-3600 cm⁻¹ also appeared, while the sample without burning treatment did not absorb during these regions.

Work by Marchese et al.[13], determined the structure of the 6.7 wt.% of coke deposited on Pt/Al₂O₃ catalysts from n-heptane reforming process, their locations, the treatment to remove them, and the structure of the metal phase after reactivation treatment. Evidences by HRTEM were coke deposits with graphitic and amorphous structures. The examination by infrared spectroscopy of the coke catalyst reactivated by oxidation at increasing temperature showed the band at 1700-1100 cm⁻¹ which disappeared by oxidation were certainly associated with coke. In particular, two correlated bands at 1580 and 1470 cm⁻¹ were due to the asymmetric and symmetric stretching vibrations of carboxylate groups, while the other components were due to deformation modes of residual

CH groups as found in carbonaceous deposits with high H/C ratio. Noticeably, bands in this region were also attributed to carbon-carbon stretching vibrations in distorted graphitic structure in dust carbon particles and in soccerball structures (C_{60} , fullerene-like molecules).

From the work of Royo et al.[14], they explained coke deposits analysis in one part using FT-IR. Catalyst coking was achieved in the dehydrogenation of butene to butadiene over a Cr_2O_3 / Al_2O_3 catalyst, at temperatures ranging from $480^\circ C$ to $600^\circ C$. The coked catalyst samples were prepared into disks with KBr of 120 mg, 1 wt.%. The results were discussed in aromatic C=C stretching zone ($1630-1500\text{ cm}^{-1}$) and the aliphatic C-H bending region ($1450-1300\text{ cm}^{-1}$). Aliphatic structure was studied in the region near 1400 cm^{-1} rather than in the 2900 cm^{-1} zone, due to strong absorption of the OH structure at 3450 cm^{-1} . The coked catalyst at $480^\circ C$ with 0.3 wt.% carbon presented a band in $1570-1520\text{ cm}^{-1}$ zone and the band at $1633-1634\text{ cm}^{-1}$ which has been assigned to stretch vibrations of the double bonds in olefinic chain. As coked catalyst temperature in dehydrogenation of butene to butadiene increased to $530^\circ C$ (1.7wt.% carbon), there was a marked increase of the 1633 cm^{-1} band, which could be attributed to the deposition on the catalyst of polyolefinic structures. A new band around 1590 cm^{-1} could be assigned to C=C bond in aromatic and highly conjugated structures. It could not be observed in the coke sample at $480^\circ C$ due to its low coke content. As the coking temperature increased from $530^\circ C$ to $580^\circ C$, the band at 1633 cm^{-1} decreased, and the band at 1590 cm^{-1} increased, which could be interpreted as an increase in the aromaticity of the coked catalysts with reaction temperature. The bands at 1400 and 1385 cm^{-1} , which corresponded to symmetric deformation of methyl groups, could be seen even with the low coke content of the sample at $480^\circ C$. The absorbance continued to increase in the coke sample at $530^\circ C$ (1.7 wt.% of carbon) and then decreased for the sample at $580^\circ C$, due to the more dehydrogenated coke obtained at this higher temperature. This suggested that aliphatic CH_3 structures presented in the coke deposits, possibly attached to aromatic structures, and they tended to disappear during the dehydrogenation process which took place at long reaction times.

2.2 Some comments on the previous work

From all of the above review, the IR spectroscopic technique has proved to be useful in defining the structure of coke deposits. The IR absorption band in the region $1000\text{-}2000\text{ cm}^{-1}$ has been frequently considered in the IR examination of coked catalysts. The characterization of carbonaceous compounds mostly attends for coked catalyst reacted in a long time on stream. Furthermore, the examination of deposited carbon always carried out on a carbon species which was isolated by dissolving away the metal and support. This seems to cause the question of whether or not the structure of extracted coke is affected by the strong acid used in such dissolution. In the case of metal/ alumina support catalyst, there are very few papers related in the IR characterization of coke deposited on this type of catalyst. However, the assignment of the characteristic functional group of coke deposited on metal/ alumina support catalyst from the IR absorption bands in the region $1000\text{-}2000\text{ cm}^{-1}$ according to the above review can be divided into two different aspects. The first aspect suggested that the IR bands in the region of $1400\text{-}1600\text{ cm}^{-1}$ were due to the carbon-oxygen stretching vibrations of the carboxylate groups. Whereas the second aspect reported that the IR bands in the region of $1400\text{-}1600\text{ cm}^{-1}$ were very specific to the presence of aromatic structure and methyl/methylene groups. Noticeable, the detection of carbon-oxygen species in coke deposits was not anticipated because coke deposition involved in reducing condition. A reasonable alternative assignment should ascribe the bands in $1400\text{-}1600\text{ cm}^{-1}$ region to the functional groups related in hydrocarbon compounds.

Accordingly, this thesis is interested in other point beyond of above review which has not been attempted that is investigation of carbon deposited on metal/ alumina support catalyst, especially in the initial stage of reaction without separation from catalyst. In this thesis, the IR absorption bands of coked catalyst are considered in the region of $1000\text{-}2000\text{ cm}^{-1}$, and the discussions of IR spectra of carbon deposits in this region deal with the species in hydrocarbon compounds in respect to the second aspect as previously stated.