CHAPTER III

THEORY

This chapter briefly describes some basic theories concerning the overview of deactivation by coking and the theoretical consideration on infrared spectroscopy.

3.1 Catalyst Deactivation

Basically, catalyst deactivation processes may be classified into three kinds [15]

1. Sintering or thermal deactivation of the catalyst
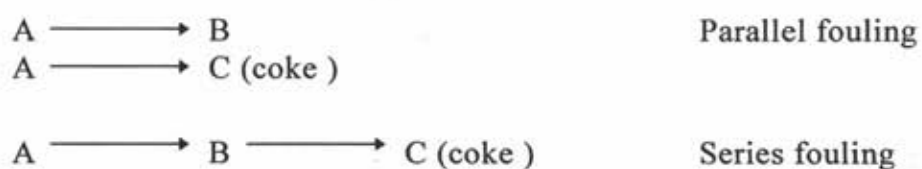
2. Poisoning

3. Fouling

While many deactivations can occur , only deactivation of catalyst caused by fouling is described in this section. The most typical of fouling process is that of the carbonaceous deposit or coke that form on most catalysts used in the processing of petroleum fractions or other organic chemical feedstocks. Unlike other causes of catalyst deactivation such as irreversible poisoning or sintering, the deactivation caused by catalyst coking can usually be reversed using relatively mild treatments. These involve removal of the coke deposits by gasification agents such as air, hydrogen, steam, or carbon monoxide, individual or in combination [16].

It is important to recognize that the coke deposit in this case originates from the reactions occurring and is not an impurity. The catalyst deactivation by coke deposition is always associated with the main reaction. Therefore, it is usually not possible to totally eliminate the coke deposition. However, coke formation can be minimized by appropriate choice of reactor and operating conditions, and in some cases by modification of the catalyst.

Examples of reactions that produce carbonaceous are extremely numerous. Virtually, any process having carbon atoms in the feed or product molecules can, under appropriate conditions ,give rise to deposition of coke. Naturally, molecules with large numbers of carbon atoms and/or those with aromatic or naphthenic rings tend to produce coke deposits more easily. Both aromatics and olefins are the immediate coke precursors which readily yield coke deposits.

Butt et al.[17] stated on the deactivation by fouling that it was strongly adsorbed carbonaceous deposits form large polynuclear aromatic structures, apparently through polymerization and condensation. However, coke is not a well-defined substance. Normally, it has an empirical formula approximating CH, but the chemical nature depends very much on how it is formed. Microscopic examination by Haldeman and Botty, which was referred by Hughes [15], established that approximately 50 % of the coke deposits were in the form of pseudo-graphitic structures with the residue probably existing as unorganized aromatic systems. It is generally agreed that the molecular formula of coke deposits varies from $C_1 H_{0.4}$ to $C_1 H_1$. Thus the coke corresponds to a hydrocarbon in composition but with only a small amount of hydrogen. The coke structure varies depending on the conditions of temperature and pressure. Moreover, these structures change as they age on the catalyst surface. Thus, it is apparent that there are great variations in the morphology of the coke depending on the catalyst and its history.

Hughes [15] noted that coking would occur in a reaction either in parallel or consecutive to the main reaction. This coke profile would be descending in the case of a parallel mechanism but ascending for a consecutive (or series) mechanism. The parallel and consecutive reactions for coking can be written as follows :

$$A \longrightarrow B$$
$$A \longrightarrow C \text{ (coke)}$$
Parallel fouling

$$A \longrightarrow B \longrightarrow C \text{ (coke)}$$
Series fouling

Thus, parallel fouling gives large coke deposits when the reactant concentration is high, since the reactant is the coke precursor. Therefore, when coking occurs by a parallel mechanism, the greatest deposition of coke would be expected at the inlet of the reactor. Conversely, larger coke deposits are formed in series fouling, when the product B has a high concentration since this is the immediate precursor of the coke in this case. In normal operation the product concentration increases with the distance along the reactor, and therefore the coke distribution should follow a similar pattern.

3.2 Infrared Absorption Spectroscopy

3.2.1 Electromagnetic Radiation

Infrared waves like X-rays, light and radio waves are classified as electromagnetic radiation since they consist of both alternating electric and magnetic fields. Each of these types of radiation has a different amount of energy. The classification of radiation according to its energy gives to electromagnetic spectrum. This is illustrated in figure 3.1.
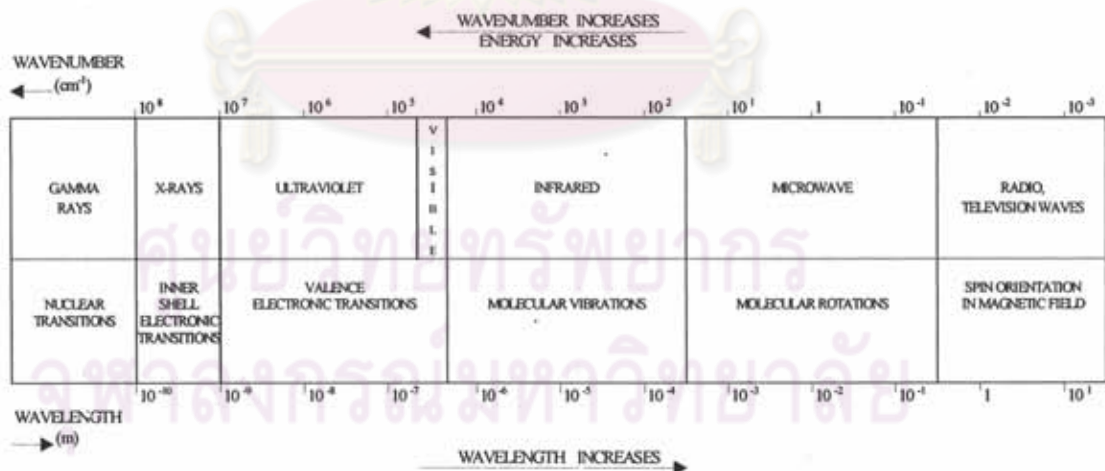

Figure 3.1 Electromagnetic Spectrum [18]

The classical description of electromagnetic radiation can be described in terms of wavelength and frequency.

The wavelength, λ, of radiation is the distance between two successive maxima or minima of the wave motion ..

The frequency, ν, is defined as the number of cycles which pass a given point per unit of time, in unit of sec^{-1} or hertz (Hz); 1 Hz = 1 sec^{-1}.

Wavelength and frequency are interrelated according to the following equation :

$$\lambda = \frac{C}{\nu} \qquad (eq.\ 3.1)$$

where: λ = wavelength (cm.)

C = velocity of light (2.99793×10^{10} cm./sec. in vacuum)

ν = frequency (Hz)

An additional parameter is often used in vibrational spectroscopy:

The wavenumber, $\tilde{\nu}$, which is defined as the reciprocal of the wavelength, and has dimension 1/length. The relation between wavelength, wavenumber, frequency, and velocity of light is given by following equation:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{C} \qquad (eq.\ 3.2)$$

The energy of the electromagnetic radiation is proportional to its frequency and its wavenumber, as follows :

$$E = h\nu = hC\tilde{\nu} = \frac{hC}{\lambda} \qquad (eq.\ 3.3)$$

where: E = energy of electromagnetic radiation (J)

h = Planck's constant (6.626×10^{-34} J.sec)

The infrared region extends from 0.78 to 1000 µm or wavenumbers from about 12800 to 10 cm^{-1} . From the standpoint of both application and instrumentation, it is convenient to divide the infrared region into three sections as near- , mid- , and far- infrared radiation, shown in figure 3.2. The majority of

analytical applications have been confined to a spectrum of the mid- infrared region extending from 4000 to 400 cm^{-1} (2.5 to 25 μm)

region	wavelength (λ),μm	wavenumber($\tilde{v}$),cm^{-1}	frequency (ν),Hz
near	0.78 to 2.5	12800 to 4000	3.8×10^{14} to 1.2×10^{14}
middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

Figure 3.2 Infrared Spectral Regions [19]

3.2.2 Molecular Energy

In the general case a molecule can have the following types of motions [20] :

(1) translation of the whole molecule,which can be regard as translation of the center of mass.

(2) rotation of the molecule as a framework around its center of mass.

(3) vibrations of the individual atoms within the framework,which occur in such a manner that the center of mass is not changed and the framework does not rotate.

(4) motions of the electrons inside the molecule.

(5) spins of the electrons and the nuclei of the atoms.

When a molecule absorbs electromagnetic radiation there is an increase in its total energy. According to the quantum theory, only a radiation of specific energy can be absorbed by a molecule, thereby raising its energy from the ground state to an excited state. This process is shown in figure3.3 where E_1

and E_2 represent the energy of the molecule in the ground state and excited state, respectively, and E_p is the energy of the photon. The energy of transition, ΔE, is equal to the energy of the interacting photon and, thus, equal to $h\nu$. This is stated mathematically according to equation 3.4.

$$\Delta E \quad = \quad E_2 - E_1 = E_p = h\nu \qquad \text{(eq. 3.4)}$$
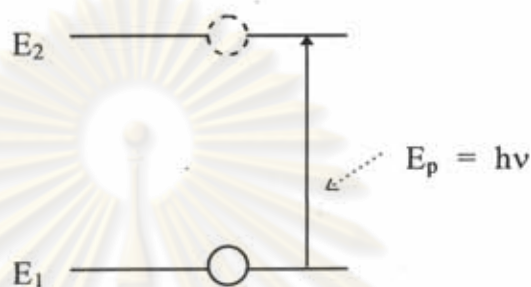

Figure 3.3   Absorption of Electromagnetic Radiation [18]

The total energy of a molecule is comprised of electronic, vibrational, rotational and translational energies. That is

$$E_{total} \quad = \quad E_{trans} + E_{rot} + E_{vib} + E_{elect.}$$

The energy involved in the transition from the electronic ground state to the first excited electronic state of a molecule usually requires radiation of greater energy than that available in the infrared region of the electromagnetic spectrum. Therefore, electronic energies usually do not have to be considered in discussion the theory of infrared spectroscopy.

3.2.3 Degree of Freedom and Molecular Motions

The remaining of a molecule are due to vibrational, rotational, and translational motions associated with the molecule. These molecular motions are commonly referred as degrees of freedom. For every atom in molecule there are three degrees of freedom corresponding to motions along the three mutually perpendicular x, y, and z coordinates in space. For nonlinear molecule containing N atoms, there will be 3N degrees of freedom: three translational, three rotational, and the remainder, 3N-6, will be vibrational. These degrees of freedom are illustrated in Figure 3.4 .

For a linear molecule there are 3N-5 vibrational degrees of freedom since a linear molecule has only two degree of rotational freedom. No change occurs in a linear molecule because rotation about its bond axis. Of these vibrational degrees of freedom, N-1 modes will be due to stretching vibrations and 2N-4 modes will be due to deformations. For a nonlinear molecule, 2N-5 modes will be due to deformations.

Absorption of infrared radiation is thus confined largely to molecular species for which small energy differences exist between various vibrational and rotational states.

Three Degrees of Translational Freedom

Three Degrees of Rotational Freedom

3N-6 Degrees of Vibrational Freedom

Note: + indicates motion from the page toward the reader

Figure 3.4 Degrees of Freedom of a Molecule [18]

3.2.4 Dipole Changes during Vibrations and Rotations

In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. Only under these circumstances can the alternating electrical field of the radiation interact with the molecule and cause changes in the amplitude of one of its motions. For example, the charge distribution around a molecule such as hydrogen chloride is not symmetric, because the chlorine has a higher electron density than the hydrogen. Thus, hydrogen chloride has a significant dipole moment and said to be polar. The dipole moment is determined by the magnitude of the charge difference and the distance between the two center of charge. As a hydrogen chloride molecule vibrates, a regular fluctuation in dipole moment occurs, and a field is established that can interact with the electrical field associated with radiation. If the frequency of the radiation exactly matches a natural vibrational frequency of the molecule, a net transfer of energy takes places that results in a change in the amplitude of the molecule vibration; absorption of the radiation is the consequence. Similarly, the rotation of asymmetric molecules around their centers of mass results in a periodic dipole fluctuation that can interact with radiation. No net change in dipole moment occurs during the vibration or rotation of homonuclear such as O_2, N_2, or Cl_2; consequently, such compounds cannot absorb in the infrared.

3.2.5 Rotational Transitions

The energy required to cause a change in rotational level is minute and corresponds to radiation of 100 cm^{-1} or smaller (> 100μm). Because rotational levels are quantized, absorption by gases in this far- infrared region is characterized by discrete, well- define lines. In liquid or solids, intramolecular collisions and interactions cause broading of the line into a continuum.

3.2.6 Vibrational and Rotational Transitions

Vibrational energy levels are also quantized, and for most molecules the energy differences between quantum states correspond to the mid- infrared

region. The infrared spectrum of a gas usually consists of a series of closely spaced lines, because there are several rotational energy states for each vibrational state. On the other hand, rotation is highly restricted in liquids and solids; in such samples, discrete vibrational/ rotational lines disappear, leaving only broadened vibrational peaks.

3.2.7 Types of Molecular Vibrations

The relative positions of atoms in a molecule are not exactly fixed but instead fluctuate continuously as a consequence of a multitude of different types of vibrations. Vibrational transitions or fundamental modes of vibration are classified as stretching modes and deformation modes. Stretching modes are described as a continuous change in the interatomic distance along the axis of the bond between two atoms and deformation modes as a change in the angle between two bonds and are of four types : scissoring , rocking , wagging and twisting. The fundamental modes of vibration are shown in figure 3.5.

Symmetric   Asymmetric

(a) Stretching vibrations

In - plane rocking   In - plane scissoring

Out - of - plane wagging   Out - of - plane twisting

(b) Bending Vibrations
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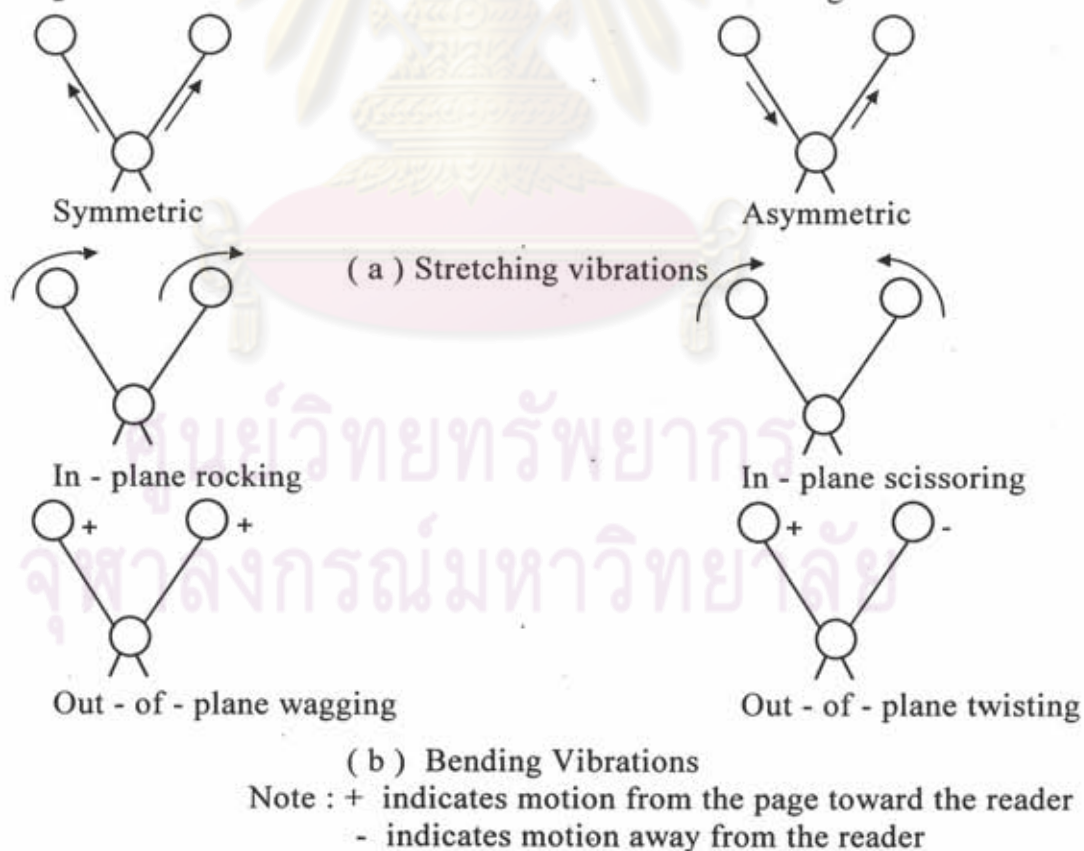   - indicates motion away from the reader

Figure 3.5 Types of Molecular Vibrations [19]

All of the vibration types may be possible in a molecule containing more than two atoms. In addition, interaction or coupling of vibrations can occur if the vibrations involve bonds to a single central atom. The result is a change in the characteristics of the vibrations involved.

3.2.8 Theoretical Considerations

As a heteronuclear molecule vibrates, the interatomic distance between atoms changes as does its dipole moment. The vibrating molecule produces an alternating dipolar electric field. The magnitude of this alternating dipolar electric field changes periodically with time at a frequency equal to the vibrational frequency. It is this dipolar electric field which interacts with the electrical component of the electromagnetic radiation giving rise to the absorption of energy. This absorption of electromagnetic radiation is what observed when recording an infrared spectrum.
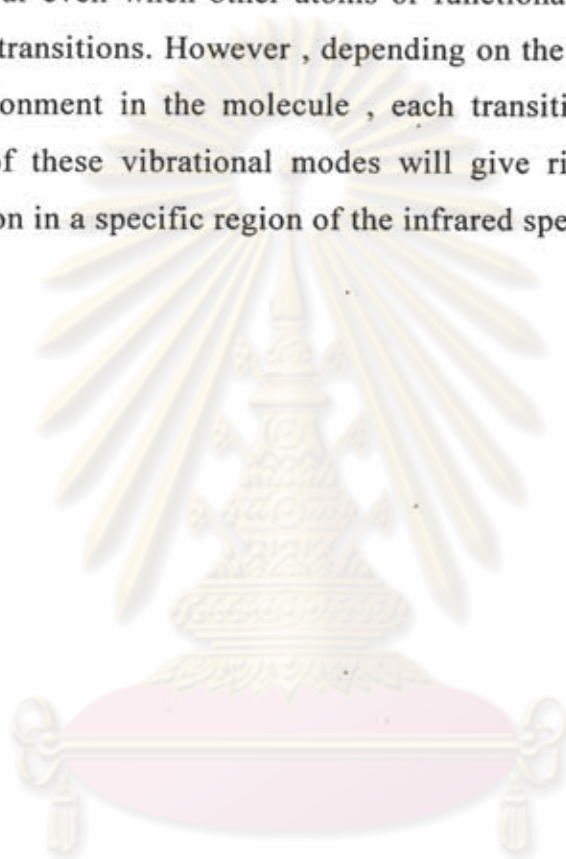
If a diatomic molecule is homonuclear, there is no change in dipole moment with the vibration and no alternating dipolar electric field is produced. Thus, the molecule does not interact with or absorb infrared radiation.

Whenever a change in dipole moment occurs, the fundamental vibration is said to be infrared active. When a vibrating molecule produces no change in its dipole moment because of symmetry, the fundamental vibration is said to be infrared inactive.

In molecules with a high degree of symmetry, many of the vibrations may occur between groups of atoms with the same reduced mass and the same force constant. These vibrations will have the same frequency and will be superimposed on the spectrum. When this occurs, the vibrations are said to be degenerate. In symmetrical molecules several modes of vibration may occur at identical frequencies, such as the three asymmetric C-H stretching vibrations in CH_3Cl. Also, many normal modes of vibration can nearly identical frequencies, such as the CH_2 vibrations in linear polyethylene. In cases like these, symmetry does not require the frequencies to coincide; however, due to chemical considerations, the adsorption bands overlap. Thus a highly symmetrical

molecule of many atoms, such as benzene, will give a simple infrared spectrum because many of its modes of vibration are degenerate. Also, the spectra of polymers can appear simpler than expected due to the accidental degeneracy of the chemically similar groups.

Vibrational motions , both stretching and deformation of any particular atom pair , occur even when other atoms or functional groups are involved in the vibrational transitions. However , depending on the types of atoms involved and their environment in the molecule , each transition will have a specific energy. Each of these vibrational modes will give rise to the absorption of infrared radiation in a specific region of the infrared spectrum.