# CHAPTER II
LITERATURE REVIEW

2.1 Chloronitrobenzenes

Chloronitrobenzenes (CNBs) are important starting organic materials for manufacture of azo and sulfur dyes, and they are extensively used in the synthesis of pesticides, fungicides, pharmaceuticals, preservatives, photochemicals and rubber chemicals. CNBs have three isomers, which are ortho, meta and para as shown in Figure 2.1.

o-CNB m-CNB p-CNB

2-chloronitrobenzene   3-chloronitrobenzene   4-chloronitrobenzene
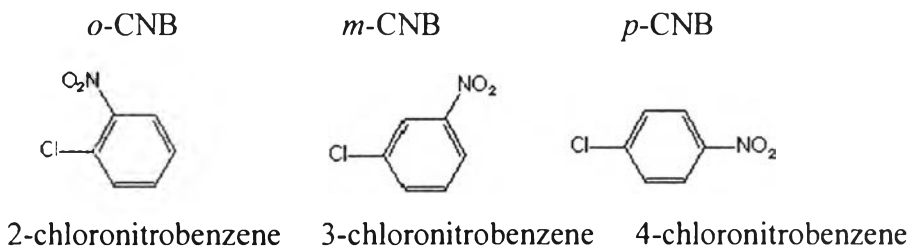
Figure 2.1 Three isomers of CNBs (orgchem.colorado.edu).

The desired isomer products depend on the reaction. There are many processes to produce CNBs. Two main processes are nitration of chlorobenzene (CB) and chloronation of nitrobenzene (NB).

Nitration of CB always gives a mixture of about one-third o-CNB and two-thirds p-CNB. The bulk of the para compound crystallizes out on cooling and can be obtained simply by centrifuging. The residual mixture cannot be separated into its constituents by fractional distillation alone because the boiling points lie too close together. However, careful fractionation through an efficient column yields a first fraction enriched in the para isomer, and a last fraction enriched in the ortho isomer. The pure compounds can be isolated from these by cooling and crystallizing, and then centrifuging. In large scale operations, the noncrystallizing middle fractions and the eutectic mixture from the centrifuging operation are put back in the process so that the separation is finally complete.

For nitration, it is customary to use a mixture of sulfuric acid, nitric acid and water. Under these conditions, the proportion of the para isomer is very high. The ratio of p- to o-CNB is usually about 1.95. Additionally, a considerable proportion of waste sulfuric acid contaminated with organic compounds is produced, requiring complicated and expensive work-up. There is a particularly high demand for o-CNB, which is obtained in the customary nitration of CB in about 35%. p-CNB, too, has a number of industrial uses.

Chlorination of NB in the laboratory requires very careful operation and succeeds only if the reaction is carried out in the complete absence of moisture. Even traces of water prevent the chlorination or retard it excessively. It is essential, therefore, that the apparatus and the starting materials be dried thoroughly. Anhydrous ferric chloride is the most satisfactory chlorine carrier. The commercial material is heated under reduced pressure in a round-bottomed flask through which a gentle stream of dry chlorine or hydrogen chloride is drawn. When the material begins to sublime, it is transferred to a bottle with a tight glass stopper. The NB is dried by heating for several hours in a round-bottomed flask at 80-100°C. While a stream of dry air is drawn through it by means of a wide capillary tube (David and Blangey, 1949).

2.2 Purification technology

Separation techniques for each isomer of CNBs are adsorption, crystallization, and crystallization followed by fractionation. The product yields of each isomer depend on the reaction that takes place. Commonly, adsorption and crystallization are utilized in many commercial processes. For example, Phillips Petroleum Company employs crystallization and fractionation and UOP LLC applies adsorption process (Robert. 1968; James. 1980b).

Crystallization does not offer a feasible means for complete separation of these components into their pure form because at a temperature of 14°C, a mixture containing p-CNB and o-CNB forms a binary eutectic mixture having a composition of 33.5 wt% p-CNB and 66.5 wt% o-CNB. From a mixture of these isomers. only

one component is readily separated in the pure form by crystallization, depending on the composition of a mixture (Robert, 1968). Thus, the need of a eutectic depressant is eliminated by extractive crystallization procedures in order to take the mixture to the other side of the normal eutectic point, followed by removing the depressant and then crystallizing the mixture. The big disadvantage with such procedures is that the depressant is often difficult to remove and results in an impure product. However, PPG Industries apply crystallization to purify m-CNB process by solidifying a mixture of the CNB isomers in the presence of a partially miscible liquid solvent (C_2-C_6 alkylene glycol) that is at a temperature below the melting point. The solidified product can be collected by filtration to provide a produce enriched in m-CNB. It appears from the evidence that the present process is not a conventional crystallization or recrystallization process for the reason that the CNB isomers are not first dissolved in the solvent and then caused to crystallize from it (James, 1980a).

In addition, Monsanto Company improves a process for separating mixtures of chemical isomers by crystallization in the presence of water (Roberto, 1974). CNB isomers are subjected to sulfonation with oleum. o- and p-CNBs are preferentially sulfonated, resulting in water-soluble sulfonated compounds that are easily separated from the mixtures by treatment with water. When a mixture of o-CNB and p-CNB is sulfonated only o-CNB is sulfonated while the p-CNB is unchanged, whereby the two compounds are stated to be easily separable (Albert, 1957).

It is well known in the separation art that certain crystalline aluminosilicates can be used to separate hydrocarbon species from mixtures. An adsorptive separation process for separating o-, m- and p-CNB from the feed mixture with an adsorbent comprises a type X or type Y zeolite containing the exchangeable cationic sites that usually are selected from the consisting of Groups IA, IIA and the transition metals of the Periodic Table of Elements. In the first adsorption stage, a selected adsorbent adsorbs substantially all o-CNB and thereafter recovering high-purity o-CNB. After that, the unadsorbed isomers are passed to a second adsorption stage where they are contacted with another selected adsorbent that selectively adsorbing substantially all

para isomers and recovering in high purity p-CNB. A desorption step may be used to desorb the adsorbed isomers in each stage (James, 1980c).

2.3 Adsorption

Liquid phase adsorption consists of two main pathways: adsorption and desorption. Adsorption of liquid adsorbate onto an adsorbent is dictated by the characteristics of the adsorbate-adsorbent interaction. Desorption depends on the addition of a desorbent and its specific interactions with both adsorbent and adsorbate. Liquid phase adsorption mechanisms are highly complex. This is due to the interaction of solid adsorbents, liquid adsorbates, and liquid desorbents during the separation process. By contrast, other convention separation process mechanisms are based primarily on the differences in the physical properties of the components. In the liquid phase adsorption matrix, a virtually infinite variability in liquid separation can be achieved as a result of the number of ways available for adsorbent and desorbent modification. Adsorbent variables include the framework structure, the counter exchange ion, and water content. These variables are carefully modified to selectively adsorb one particular component over others. To desorb the adsorbed component, a suitable solvent functioning as a desorbent first needs to be identified (Kulprathipanja and Johnson, 2002).

The selectivity may depend on a difference in either adsorption kinetics or adsorption equilibrium. But most of the adsorption processes in current use depend on equilibrium selectivity. In considering such processes, it is convenient to define a separation factor:

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B} \tag{2.1}$$

where X_A and Y_A are, respectively, the mole fractions of component A in adsorbed and fluid phases at equilibrium. The separation factor defined in this way is precisely analogous to the relative volatility, which measures the ease with which the components may be separated by distillation. The analogy is, however, purely formal and there is no quantitative relationship between the separation factor and relative

volatility. For two given components, the relative volatility is fixed whereas the separation factor varies widely depending on the adsorbent (Ruthven, 1984).

2.3.1 Equilibrium-selective adsorption

To achieve the liquid phase adsorption separation, one has to balance two opposing forces: the adsorptive force of the adsorbent to a component and the desorptive force of the desorbent. Although there is complexity in liquid phase adsorption mechanisms, they can be classified into five broad categories: equilibrium-selective adsorption, rate-selective adsorption, shape-selective adsorption, ion exchange, and reactive adsorption.

The foundation of equilibrium-selective adsorption is based on the difference in phase compositions at equilibrium. While all the adsorbates have access to the adsorbent sites, the adsorbate are selectively adsorbed based on differences in the adsorbent-adsorbate interaction. An advantage of using an adsorbent as a separation agent is that for each particular separation, equilibrium phase relations can be critiqued and developed to find the most favourable conditions. This is particular true of synthetic zeolites and resins containing exchangable cations. Anions are also involved in the case of resins, and must be considered. In some cases, amorphous oxides and activated carbon can be developed to achieve this mechanism. Zeolites represent an important group of adsorbents being used in most commercial liquid separation process. This is due to the high selectivity and adsorption capacity of zeolite adsorbents.

Equilibrium-selective adsorption effects depend on the magnitude of the dispersion, repulsion, and electrostatic force of adsorbent-adsorbate interactions. The selectivity of zeolites is influenced by the following physical characteristics of each zeolite: the exchanged metal cation, the ratio of SiO_2/Al_2O_3, and water content. Adsorbent selectivity is also controlled by the desorbent used to desorb the adsorbed component from the adsorbent. The operating temperature is another parameter that can alter the adsorbent selectivity.

Zeolites can be ion-exchanged with a variety of metal cations to alter their acidity. There is a strong correlation between the total acidity of a zeolite (the sum of Bronsted and Lewis acidity) and the ion radius or valence of the exchanged

cation. Exchanged cations with a lower ionic radius give higher zeolite acidity. Zeolite acidity increases for monovalence exchanged cations from Cs < K < Na < Li and increases for divalence exchanged cations from Ba < Pb < La < Ca < Zn < Co. For cations of similar ionic radii, divalence cations give higher zeolite acidity than monovalence cations.

Zeolites acidity is also determined by the SiO_2/Al_2O_3 ratio of the zeolite. As would be expected, zeolite acidity increases as the ratio of SiO_2/Al_2O_3 decreases. This is caused by the increase in AlO_4^- sites, which leads to strengthening the electrostatic field in the zeolite. In addition, a wide array of cage and channel arrangements and electrochemical properties result from various crystalline structures for different SiO_2/Al_2O_3 ratios. Manipulating both the exchanged cation and the SiO_2/Al_2O_3 ratio offers a greater flexibility in tailoring adsorbents for a specific application. However, by altering multiple variables, the absorption behavior becomes more complex and difficult to predict than if based solely on the acid-base interaction mechanism.

Adsorbed water molecules on a zeolite are polarizable due to a strong electrostatic field between the exchanged cations and alumina framework. As can be anticipated, water molecules will enhance the zeolite Bronsted acid properties. Adsorbate-adsorbent interaction, and in turn, adsorbent selectivity, will thus be altered due to water polarization.

In the liquid phase adsorption process, the solid zeolite adsorbent will interact with liquid adsorbates and liquid desorbents. At equilibrium, the liquid composition within the zeolite pores differs from that of the liquid surrounding the zeolite. These compositions can be related to each other by enrichment factors for adsorbent selectivity. The more selective component is more likely to be concentrated in the pores than in the surrounding liquid.

A less critical factor than those previously discussed is the operation temperature. However, the liquid phase adsorptive separation process must be operated at a temperature that balances selectivity and transfer rate. Generally, selectivity will increase at lower temperatures. However, this increase is at the expense of the transfer rate of the system.

2.3.2 Rate-selective adsorption

In addition to being evaluated based on phase compositions at equilib-rium, an adsorptive separation process may also be evaluated based on the diffusion rates through a permeable barrier. These evaluations are designated as "rate-selective adsorption" processed. In some instances, there may be true equilibrium selectivity as well as rate selectivity.

A rate-selective adsorption process will not yield a good separation unless the diffusion rates of the feed components differ by a wide margin. For exam-ple, the smaller kinetic diameter components will have a higher diffusion coefficient. This usually gives better selectivity than bigger kinetic diameter components.

2.3.3 Shape-selective adsorption

Equilibrium- and rate-selective mechanisms deal with adsorbate-absorbent interactions and molecular diffusion rates through zeolite pores. Shape-selective adsorption is a process that separates molecules that can enter the adsorbent pores from ones that are completely excluded. Thus, selectivity of the entered com-ponents with respect to the excluded components is infinite.

2.3.4 Ion exchange

Ion exchange separation is defined as the reversible exchange of ions between a solid adsorbent and a liquid adsorbate, in which there is no substantial change in the structure of the solid adsorbent. The solid adsorbent is composed of a large number of ionic (or potentially ionic) sites such as zeolites and ion exchange resins. An ion exchange resin is elastic, three-dimensional hydrocarbon network at-tached by a large number of ionizable groups. For most zeolites, the aluminosilicate portion of the structure is a three-dimensional open framework consisting of a net-work of AlO_4^{-5} and SiO_4^{-4} tetrahedrons linked to each other by oxygen molecules. The framework contains channels and interconnected voids occupied by cations and water molecules. The cations are quite mobile and can usually be exchanged by other cations to varying degrees.

2.3.5 Reactive adsorption

Reactive separation processes are unique in that they combine the normally unit operations of reaction and separation into a single, simultaneous operation. The advantages of such technology are principally in energy and capital cost reduction, as well as in increased reaction efficiency. Additionally, reactive separation is sometimes the only method by which effectively separate species when conventional means such as adsorption, distillation, or extractions are not applicable.

Reactive adsorption is characterized by simultaneous chemical reactions and separations. In a singer reactor-separator vessel, it is possible to obtain high purity products directly from the reactor, with downstream purification requirements greatly reduced or even eliminated. These can result in reduced design complexity and capital costs.

2.4 Zeolite

Zeolites represent an important group of adsorbents being used in most commercial liquid separation processes. This is due to the high selectivity and adsorption capacity of zeolite adsorbents. Zeolites are crystalline aluminosilicates of alkali or alkali earth elements, such as sodium, potassium, and calcium, and are represented by the chemical composition:

$$M_{x/n} [(AlO_2)_x (SiO_2)_y] . zH_2O$$
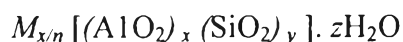
where x and y are integers with y/x equal to or greater than 1, n is the valence of cation M, and z is the number of water molecules in each unit cell. The primary structural units of zeolites are the tetrahedra of silicon and aluminum, SiO_4^{-4} and AlO_4^{-5}. These units are assembled into secondary polyhedral building units such as cubes, hexagonal prisms, octahedra, and truncated octahedra. The silicon and aluminum atoms, located at the corners of the polyhedra, are joined by shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three-dimensional crystalline framework. The tetrahedral can be arranged in numerous ways, resulting in the possibility of some 800 crystalline structures, less than 200 of which have been found in natural deposits or synthesized in laboratories around the world (Thompson, 1998). The void delimited by the aluminosilicate ske-

leton is organized into a network of cavities connected by pores of uniform size. The effective pore diameter, variable depending on the type of zeolite, is of the same order of magnitude (3 to 10 Å) as that of most organic molecules. This explains the name "molecular sieve" given to these adsorbents (Wauquier, 2000).

Types A, X, and Y remain the dominant zeolites and molecular sieves that are in commercial use for adsorption and ion exchange. These zeolites will be the main subject for discussion.

2.4.1 Type X and Y zeolites

Unit cells of type X and type Y zeolites are shown in Figure 2.2. The cations are necessary to balance the electric charge of the aluminum atoms in AlO_4^{-5}, each having a net charge of -1. The water molecules can be removed with ease upon heating and evacuation, leaving an almost unaltered aluminosilicate skeleton with a void fraction between 0.2 and 0.5. The skeleton has a regular structure of cages, which are interconnected by windows in each cage. The cages can imbibe or occlude large amounts of guest molecules in place of water. The size of the window apertures, which can be controlled by fixing the type and number of cations, ranges from 3 to 8 Å. The sorption may occur with great selectivity because of the size of the aperture (and to a lesser extent due to the surface property in the cages). The windows of type X zeolite are referred to as 12-ring, which remain the largest windows in zeolites today (Yang, 2003).

(a)   (b)
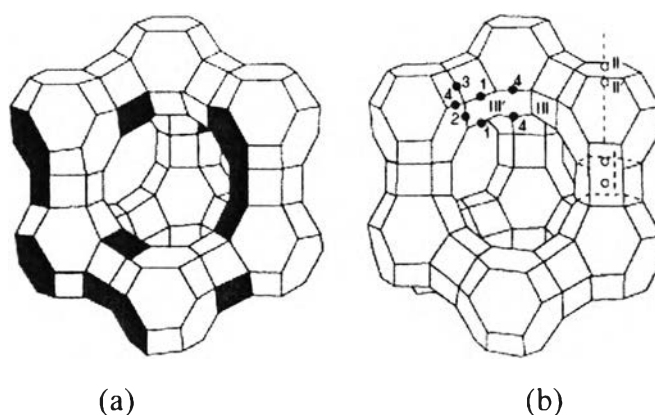
Figure 2.2 Line representations of zeolite structure: (a) 'unit cell' of types X and Y, or faujasite ; (b) cation sites in types X and Y (16 I, 32 I', 32 II, 32 II', 48 III, and 32 III' sites per unit cell) (Yang, 2003).

The ratio of Si/Al in types X and Y are typically one to five. The aluminum atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations. The cations can also be exchanged. The inner atoms in the windows are oxygen. The sizes of the windows then depend on the number of oxygen atoms in the ring (4, 5, 6, 8, 10, or 12). A description of the structures will be given for the zeolites, types X and Y, important in gas separation. As mentioned, these types have dominated the commercial use of zeolites for gas separation and purification as well as ion exchange since their invention.

The skeletal structure of types X and Y zeolites is the same as naturally occurring faujasite. The sodalite units are linked through 6-member prisms, as shown in the unit cell in Figure 2.2. Each unit cell contains 192 (Si, Al)O_4 tetrahedra. The number of aluminum ions per unit cell varies from 96 to 77 (i.e., Si/Al = 1 to 1.5) for type X zeolite, and from 76 to 48 (Si/Al = 1.5 to 3) for type Y zeolite. Loewenstein's rule forbids the formation of Al-O-Al bridges (Loewenstein, 1954). Thus, the maximum number of Al corresponds to a Si/Al ratio of 1. Kuhl (1987) reported a procedure for the synthesis of the low-silica X (LSX) zeolite (with Si/Al = 1). At Si/Al > 3, they are named USY (i.e., ultra-stable Y). The Si/Al ratio in the commercial USY zeolite can be very high like 195. The framework of faujasite has the largest central cavity pore volume of any known zeolite, amounting to about 50% void fraction in the dehydrated form. The free diameter of the central cavity is

13.7 Å (Eulenberger *et al.*, 1967). A unit cell, when fully hydrated, contains approximately 235 water molecules, primarily in the central cavity. The volume of the central cavity, however, accounts for only a small fraction (1/5–1/8) of the pore volume of the unit cell since there are portions of other central cavities from the neighboring unit cells, as well as window spaces that are also contained in the same unit cell. The aperture is formed by the 12-member oxygen rings with a free diameter of approximately 7.4 Å. The size of the unobstructed 12-ring is approximately 8.1 Å (Breck, 1974). Three major locations for the cations are indicated in Figure 2.2b. The locations are center of the 6-member or hexagonal prism (I) and opposite to I and located in the sodalite cage (I'), similar to I and I' but further from the central cavity (II and II'), and the 12-ring aperture (III and III'). The commercial 10X zeolite contains Ca^{+2} as the major cation, and Na^+ is the major cation for 13X zeolite. The BET surface area measured with N_2 for zeolites falls in the range between 500 and 800 m^2/g (Yang, 2003).

2.4.2 Zeolites as adsorbents

The unique channels and high surface area of zeolites or zeolite-type materials provide these materials with a high adsorption capacity and shape-selective adsorption. Zeolites have been used as desiccants for drying air, natural gas, other light hydrocarbon gaseous streams, and some liquid streams to remove water. Zeolites have a high adsorption capacity of moisture and a strong power to remove water from gases. The dew-point of a gas steam can be achieved to below $-100°C$. For example, in the cryogenic separation of the hydrocarbons in a steam cracker of naphtha, zeolite A is used to remove trace amounts of water in the hydrocarbon stream to achieve a low dew point to avoid blocking of pipelines which may happen due to freezing water.

Zeolites are also used for separation or purification. For instance, zeolite Ag-X is used to recover ethylene from a dilute ethylene stream; zeolite A is used to remove water, CO_2 and H_2S from natural gas; zeolite X is used to remove aromatics from naphtha; zeolite A is used for separation of oxygen and nitrogen from air; ZSM-5 is used in separation of para-xylene from a C_8 aromatic hydrocarbon mixture; zeolite A is used to separate normal paraffins from their isomers. Some other

recent applications of zeolites as adsorbents may be found in environmental control and protection, such as in the application of catalytic converters in automobiles, removal of volatile organic compounds from air, and odor control in restrooms (Fougerit *et al.*, 1994).

When zeolites are used for separation or purification, the molecule to be removed or separated should have a difference in one or more of the following properties from the other molecules:

♦ molecular size and shape

♦ polarity for polar molecules

♦ induced-dipole moment for non-polar molecules

♦ boiling point

♦ saturation of hydrocarbons (saturated and unsaturated hydrocarbons)

♦ aromaticity of hydrocarbons (aromatics and non-aromatics)

Theoretically, if the molecules in a mixture distinguish in one or more of the above properties, a zeolite or a modified zeolite could be found to facilitate to the separation. The zeolites used as adsorbents are mainly A and X type zeolites. About six percent of synthetic zeolites in the world are used as adsorbents.