CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Background

2.1.1 Adsorption

Consider a heterogeneous system composed a fluid phase (liquid or gaseous) and a solid surface. Further assume that the fluid phase is a solution of several different chemical species and that the fluid and solid phases are under thermodynamic equilibrium. A species present in the fluid phase is said to be adsorbed on the solid surface if the concentration of the species in the fluid-solid boundary region is higher than that in the bulk of the fluid. Adsorption takes place because of the interaction between the species present in the fluid phase and solid surface.

It is obvious that adsorption is a surface phenomenon and that its definition rests upon concentration measurements and carries no implications of mechanisms. The species that is adsorbed is called adsorbate. There may be one or more adsorbates in a given adsorption situation. Adsorption-based separation processes, which are developed to separate or purify homogeneous mixtures, operate on the principle of difference in adsorption potential (Ruthven, 1984).

2.1.2 Selectivity

The primary requirement for an economic separation process is an adsorbent with sufficiently high selectivity, capacity, and life. The selectivity may depend on a difference in either adsorption kinetics or adsorption equilibrium. In considering such processes, it is convenient to define a separation factor:

$$\alpha_{AB} = \frac{X_A/X_B}{Y_A/Y_B} \qquad (2.1)$$

where X_A and Y_A are, respectively, the mole fractions of component "A" in the 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).

2.1.3 Liquid Phase Adsorption Mechanisms

As all experiments in this work were performed in liquid phase, information related to liquid phase adsorption mechanisms are provided here.

Liquid phase adsorption mechanisms are highly complex (Kulprathipanja and Johnson, 2001). This is due to the interaction of solid adsorbents, liquid adsorbates, and liquid desorbents during the separation process. By contrast, other conventional 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. 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 the 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.

2.1.3.1 Equilibrium-Selective Adsorption

The foundation of equilibrium-selective adsorption is based on the differences in phase compositions at equilibrium. While all the adsorbates have access to adsorbent sites, the adsorbates are selectively adsorbed based on differences in the adsorbate-adsorbent interaction. Equilibrium-selective adsorption depends on

the magnitude of the dispersion, repulsion, and electrostatic forces of adsorbate-adsorbent interactions. To achieve a meaningful separation, the adsorbent is manipulated to obtain a larger interaction, selectively, for one component of a mixture.

2.1.3.2 Rate-Selective Adsorption

In addition to being evaluated based on phase compositions at equilibrium, 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" processes. 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 example, the components that have smaller kinetic diameters, in turn, having a higher diffusion coefficient, usually yield better selectivity than bigger kinetic diameter components.

2.1.3.3 Shape-Selective Adsorption

Equilibrium- and rate-selective mechanisms deal with adsorbate-adsorbent interactions and molecular diffusion rates through adsorbent 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 components with respect to the excluded components is infinite.

2.1.3.4 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-dimentional hydrocarbon network attached by a large number of ionizable groups. For most zeolites, the aluminosilicate portion of the structure is a three-dimentional open framework consisting of a network of AlO_4 and SiO_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.

2.1.3.5 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 reductions, 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 extraction are not applicable.

Reactive adsorption is characterized by simultaneous chemical reactions and separations. In a single 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.

2.1.4 Zeolites

Zeolites are microporous inorganic compounds with their crystal structures containing large pores and voids. Effective pore sizes in microporous solids range from 3 Å to over 10 Å, sufficient to permit the diffusion of organic molecules. This feature gives rise to many important applications of the materials.

The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions, into which guest molecules can penetrate. Because the micropore structure is determined by the crystal lattice, it is precisely uniform with no distribution of pore size. This feature, which distinguishes the zeolites from traditional microporous adsorbents, is micropore structure.

In considering the zeolite framework, it is convenient to regard the structure as a built up from assemblages of secondary building units. The secondary building units and some of the commonly occurring polyhedra, which consists of several SiO_4 and AlO_4 tetrahedra, are shown schematically in Figure 2.1. In the

diagrams, each vertex represents the location of a *Si* or *Al* atom while the lines represent, approximately, the diameters of the oxygen atoms or ions, which are very much larger than the tetrahedral *Si* or *Al* atoms.
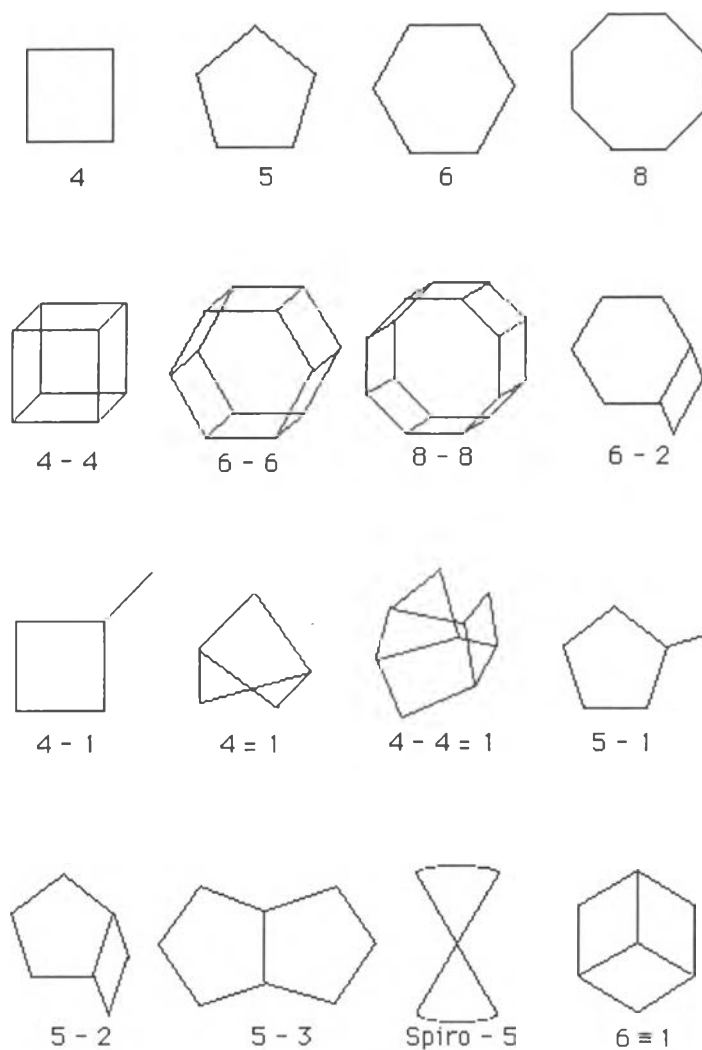
Figure 2.1 Secondary building units and commonly occurring polyhedral units in zeolite framework structure (http://www.kjemi.uio.no/~pouln/cspositions.html)

Each aluminum atom introduces one negative charge on the framework, which must be balanced by an exchangeable cation. The exchangeable cations are located at preferred sites within the framework and play a very important role in determining the adsorptive properties. Changing the exchangeable cation by ion exchange provides a useful means of modifying the adsorption properties.

The synthetic zeolites X and Y, the zeolites used in this work, and the natural zeolite faujasite all have the same framework structure, which is sketched in Figure 2.2. The crystallographic unit cell consists of an array of eight cages containing a total of 192 AlO_4 and SiO_4 tetrahedral units. The framework may be thought of as a tetrahedral lattice of sadalite units connecting through six-membered oxygen bridges, or equivalently as a tetrahedral arrangement of double six-ring units. The resulting channel structure is very open with each cage connected to four other cages through twelve-membered oxygen rings of free diameter 7.4 Å. Large molecules such as neopentane and tertiary butyl amine can penetrate these pores.
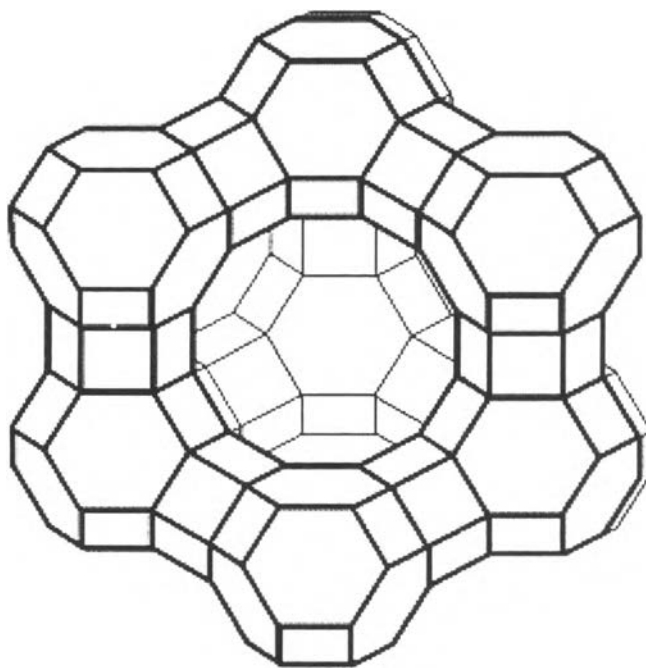
Figure 2.2 Schematic representation showing framework structure of zeolite faujasite (http://Chemmac1.usc.edu/bruno/zeodat/Intro.html)

The difference between X and Y zeolites lies in the Si/Al ratio, which is within the range 1-1.5 for X and 1.5-3.0 for Y. There is a corresponding difference in the number of exchangeable univalent cations, which vary from about 10-12 per cage for X to as low as 6 for high silica Y. The distribution of the cations between the various sites depends both on the nature and number of the cations and is affected by

the presence of traces of moisture. The adsorptive properties of X and Y zeolites may therefore be greatly modified by ion exchange and improvement selectivity can sometimes be obtained by using mixed cationic forms.

2.1.5 General Statistical Model

The generalized statistical model has been successfully applied to the correlation of liquid phase adsorption equilibrium data for C_8 aromatics on faujasite zeolites (Ruthven, 1984, Varanyanond, 2001). For these systems, the saturation limit corresponds to approximately three molecules/cage, and at equilibrium with the liquid the adsorbent is essentially saturated so that each cage can be assumed to contain three sorbate molecules. The expression for the separation factor, assuming an ideal binary fluid phase then becomes

$$\frac{\alpha_{12}}{k_1/k_2} = \frac{1 + 2A_{21}\left(\frac{k_2 Y_2}{k_1 Y_1}\right) + A_{12}\left(\frac{k_2 Y_2}{k_1 Y_1}\right)^2}{\left(\frac{k_2 Y_2}{k_1 Y_1}\right)^2 + 2A_{12}\left(\frac{k_2 Y_2}{k_1 Y_1}\right) + A_{21}} \tag{2.2}$$

where Y is the mole fraction in the liquid phase, k is the equilibrium constant, A is the interaction coefficient, and α is the separation factor.

For the studied system, it is reasonable to assume that no interaction between molecules, therefore $A_{12}=A_{21}$. By combining equation (2.1) and (2.2) together, the expression then becomes:

$$\alpha_{12} = k_1/k_2 = \frac{X_1/X_2}{Y_1/Y_2} \tag{2.3}$$

The solver function in Microsoft excel program is applicable to obtain the most suitable parameters from experimental data.

2.2 Literature Survey

The adsorption amount of xylenes is dependent on the ionic radius of the exchanged cation. The adsorption capacity is higher for the zeolites exchanged with a mono-valent small cation. It was found that the total acidity of zeolite has a strong correlation with the ionic radius or valance of exchanged cation. A small ionic radius or large valencies of exchanged cation results in strong acidity of the zeolite. The higher acidity, the lower adsorption capacity of zeolite. Moreover, the acidity of zeolite depends on the ratio of SiO_2/Al_2O_3 and moisture content. As this ratio increases or the moisture content decreases, the acidity of zeolite decreases (Seko, 1980).

Barthomeuf and Mallmann (1990) found that the selectivity in the separation of C_8 aromatics by adsorption might involve different types of interaction. m-xylene, which is the most basic of the four C_8 isomers, preferentially interacts with Na ion. Therefore, NaY, which places in the range of acidity zolites is selective for m-xylene, whereas KY, which is selective for p-xylene, a less basic isomer, is in the range of slightly basic materials.

Besides the faujasite type zeolites, ZSM-5 was tested for the separation of p-xylene and ethylbenzene from the C_8 aromatics mixture by Tsoung (1989). The total adsorption capacity of ZSM-5 is between 160 and 190 mg/g. ZSM-5 with a high SiO_2/Al_2O_3 ratio is highly selective for p-xylene, and the selectivity for p-xylene over ethylbenzene can be as high as 5.5. The competitive adsorption capacity for p-xylene from a typical xylene mixture is 120 mg/g. The high p-xylene selectivity and dependence on the p-xylene loading are believed to be related to the unique packing of p-xylene in the crystalline cavities. The author pointed out that the presence of moisture affects the selectivity for p-xylene and also adsorption capacity of low silica ZSM-5 but not for high silica ZSM-5. If the water content in the low silica ZSM-5 is high, the selectivity for p-xylene decreases.

It has been shown by Bellat et al. (1997) that, at 25°C, the adsorption processes of p-xylene and m-xylene on Y zeolite are not different The adsorption capacities of α-cages are nearly the same for the two xylenes and do not change by

cation exchange with potassium or barium. Despite the fact that the external surface of faujasite is small (~17 m^2/g), the amount of xylene adsorption is significant, up to 13% of the total amount adsorbed at saturation. It is twice as much with m-xylene as with p-xylene. However, some variations of the adsorption capacities were observed according to the nature of compensation cation, temperature and pressure.

At the high temperature and low pressure, Bellat *et al*. (1997) found that the adsorption capacities of *BaY* are greater than *NaY* and *KY* zeolites. Thus, *BaY* zeolite shows a stronger adsorption affinity for xylene than *NaY* and *KY* zeolites. Both *NaY* and *KY* zeolites have a similar behavior and adsorb a little more of m-xylene than p-xylene. At the low temperature and high pressure, *KY* zeolite has the same behavior as *NaY* zeolite with p-xylene and as *BaY* zeolite with m-xylene. Inversely, like *NaY* zeolite, the adsorption capacities of *KY* and *BaY* zeolites are greater for p-xylene than for m-xylene.

Cottier *et al*. (1997) found that the selectivity of *Y* zeolite depends on the filling, the composition of the mixture, and the exchangeable cation. Two selectivity adsorption processes are discerned according to the filling of α-cages. For the filling lower than 2 molecules/α, *BaY* and *NaX* exhibit the same behavior toward the coadsorption of p-xylene and m-xylene and adsorb preferentially the more abundant isomer in initial adsorptive mixture: the selectivity depends only on the composition of the mixture. For the filling higher than 2 molecules/α, *BaY* is more selectivity for p-xylene and independent of the adsorptive mixture composition whereas *NaY* is selective for m-xylene. The selectivity depends on the exchangeable cation. The dependence of the adsorbate composition on the selectivity shows a non-ideal behavior of the adsorbate.

The study on the C$_8$ aromatics adsorption on faujasite zeolites by Iwayama and Suzuki (1994) pointed out that the adsorption selectivity for C$_8$ aromatics on faujasite depends on the electron density of adsorption site, which is affected by the interaction between metal ion and *AlO$_4$*. The adsorption selectivity for p-xylene, which is the less basic, increases in the order *LiY*, *NaY* and *KY*. Moreover, the adsorption selectivity for p-xylene on *KY* depends on its *SiO$_2$/Al$_2$O$_3$* ratio. As this ratio increases from 3.2 to 5.5, the amount of metal ion in the unit cell decreases and

the packing of p-xylene in the supercage becomes easier, enhancing the selectivity for p-xylene.

Barthomuef (1991) tried to relate the acidity of X and Y zeolites exchanged with Li, Na, K, Rb, and Cs to the intermediate electronegativity of a substance, S_{int}. The higher the S_{int}, the higher the acidity of a zeolite. Table 2.1 presents the S_{int} of each zeolite.

Table 2.1 The intermediate electronegativity of X and Y zeolites exchanged with mono-valence cations, S_{int} (Barthomuef, 1991)

zeolites	S_{int}
CsX	2.88
RbX	2.97
KX	3.03
NaX	3.23
LiX	3.26
CsY	3.27
RbY	3.33
KY	3.39
NaY	3.51
LiY	3.56

Although there is no fundamental thermodynamic difference between liquid and vapor adsorption because the composition of an adsorbed phase in equilibrium with a liquid must be precisely the same as that which is in equilibrium with the corresponding saturated vapor, kinetics is responsible for the main difference between the adsorption in liquid phase and gas phase. Mass transfers to the adsorption sites are much slower in the liquid phase, but the adsorption capacities and the selectivity are of the same order of magnitude. They depend only on the nature of the compensation cation in the silica alumina ratio and the water content. However, a qualitative difference arises because vapor phase adsorption studies are

generally carried out at a relatively low loading whereas in the liquid phase adsorption, the total adsorbed phase concentration is always at or near the saturation limit (Hulme *et al.*, 1991).

Liquid phase adsorption of each C_8 aromatic was studied by Ngamkitidachakul (2000) using *KBaX* and *KY* in the range of 1.25-20 % wt. *KBaX* and *KY* are selective for *p*-xylene and least adsorb *o*-xylene. As the adsorption process is exothermic, the zeolites adsorb all the species less at higher temperature. But, at the full capacity of both zeolites, temperature has very little effect on the selectivity of *p*-xylene relative to the other C_8 aromatics. The author applied the following model to predict the distribution coefficient.

$$K = q/C = k + AC^m \qquad (2.4)$$

where q is solute concentration based on particle volume (g/cm^3) and C is solute concentration in bulk phase (g/cm^3). Because of the curvature of the equilibrium line is not too great, m was set equal to one. Parameter k is the apparent Henry's law constant, the slope of the equilibrium line at infinite dilution. A and k were determined by fitting the equation to the experimental data. The model fits well with the experimental data at the high temperature but there are some deviations at the low temperature.

Varanyanond (2001) has shown that the transfer rate is low at the low temperature. The liquid phase adsorption process must be operated at a temperature that balances selectivity and transfer rate. Moreover, the presence of water in zeolite affects the *p*-xylene selectivity. As water content increases, *p*-xylene selectivity declines. The experiments were carried out at the low concentration thus linear isotherm is not unexpected since it lies in the Henry's law region. The author used the simplified general statistical model, equation (2.2), to predict the constant separation factor (α_{AB}). The cross coefficient are set to unity ($A_{12}=A_{21}=1$) and the expression reduces to a constant separation factor given by equation (2.3), k_1 and k_2 were obtained from the experimental data. This simplified model fits well at the low concentration range.