



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

Background information related to this work is provided in this chapter. First, principle of adsorption and selectivity is explained in details. Zeolites are the next focus with the emphasis on *X* and *Y* zeolites. More details on adsorbents can be found in Ruthven (1984). Then, the statistical adsorption model is introduced. After that, some related work in the separation of the C_8 aromatics is discussed.

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.

2.1.2 Selectivity

An economic separation process firstly requires an adsorbent with sufficiently high selectivity, capacity, and life. The selectivity may vary with differences in either adsorption kinetics or adsorption equilibrium. The separation factor is defined as

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

where X_A and Y_A are, respectively, the mole fraction 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. However, the analogy is purely formal, and there is no quantitative relationship between the separation factor and relative volatility. For two given components, the relative volatility is fixed while the separation factor varies widely depending on the adsorbent. Because the separation factor generally depends on temperature and often also with composition, the separation factor is a major consideration in the process design. For an ideal Langmuir system, the separation factor is independent on composition and equal to the ratio of the Henry's law constants of the two relevant components. Therefore, preliminary selection of suitable adsorbents can, sometimes, be made directly from available Henry's constants.

2.1.3 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 of the most 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.

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 and widely means of modifying the adsorption properties.

The synthetic zeolites *X* and *Y* 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.

The difference between the X and Y sieves 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 sieves may therefore be greatly modified by ion exchange and improvement selectivity can sometimes be obtained by using mixed cationic forms.

2.1.4 General Statistical Model

The generalized statistical model (Ruthven, 1984) has been successfully applied to the correlation of liquid phase adsorption equilibrium data for C_8 aromatics on faujasite zeolites. 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

$$\frac{\alpha_{12}}{k_1/k_2} = \frac{1 + 2A_{21}\left(\frac{k_2Y_2}{k_1Y_1}\right) + A_{12}\left(\frac{k_2Y_2}{k_1Y_1}\right)^2}{\left(\frac{k_2Y_2}{k_1Y_1}\right)^2 + 2A_{12}\left(\frac{k_2Y_2}{k_1Y_1}\right) + A_{21}} \quad (2.2)$$

where Y is 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 $A_{12}=A_{21}$. The expression then becomes:

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

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

2.2 Literature Survey

High-silica medium-pore zeolites, such as *ZSM-5*, are excellent adsorbents for the separation of *p*-xylene and ethylbenzene from C_8 aromatics. In addition to high adsorption selectivity and capacity, the separation performance of high-silica *ZSM-5* is not affected by the presence of moisture due to its hydrophobicity. The *ZSM-5* becomes essentially hydrophobic as its SiO_2/Al_2O_3 ratio exceeds 300 (or for an Al_2O_3 content of <0.34%), and its hydrocarbon adsorption capacity and selectivity are not affected by water. Similar to conventional faujasite-based adsorbents, low-silica (high-alumina) zeolite lose hydrocarbon adsorption capacity and *p*-xylene selectivity in the presence of water (Yan, 1989).

ZSM-5 zeolite was tested for the separation of *p*-xylene and ethylbenzene from the C_8 aromatics mixture by Yan (1989). *ZSM-5* with a high SiO_2/Al_2O_3 ratio is highly selective for *p*-xylene adsorption, and the selectivity for *p*-xylene over ethylbenzene can be as high as 5.5. The total adsorption capacity of *ZSM-5* is between 160 and 190 mg/g and the competitive adsorption capacity for *p*-xylene from a typical xylene mixture is 120 mg/g. The high *p*-xylene selectivity and dependence on *p*-xylene loading

are believed to be related to the unique packing of *p*-xylene in the crystalline cavities.

Barthomeuf and Mallmann (1990) studied the adsorption of benzene and *o*-xylene by means of infrared spectroscopy on $\text{AlPO}_4\text{-5}$ and *NaY*. *NaY* is selective for *m*-xylene over the other C_8 aromatics. Since *m*-xylene is the most basic of the four C_8 isomers, it preferentially interacts with the Na^+ ion, which is acidic in the alkaline ions series. For *NaY*, the main effect is the aromatic-zeolite interaction, which disturbs the adsorbed molecules. On the other hand, the C_8 aromatics do not interact significantly with $\text{AlPO}_4\text{-5}$, but changes in the packing of these molecules alter the shape of the infrared spectra. In $\text{AlPO}_4\text{-5}$, where no adsorbent-adsorbate interactions are found, the packing of molecules and consequently their cohesive energy are important. The work shows that the selectivity in the separation of the C_8 aromatics by adsorption may involve very different types of interaction.

Hulme *et al.* (1991) examined the adsorption in a thermodynamic perspective. 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. 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 capacity and the selectivity are of the same order of magnitude. The adsorption capacity depends 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 relatively low loading whereas in the liquid phase adsorption, the total adsorbed phase concentration is always at or near the saturation limit.

At high temperature and low pressure, the adsorption capacity of *BaY* is greater than *NaY* and *KY* zeolites. Thus, *BaY* zeolite shows a stronger

adsorption affinity for *p*-xylene and *m*-xylene than those of two zeolites. *NaY* and *KY* zeolites have a similar behavior and adsorb a little more of *m*-xylene than *p*-xylene. At 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 capacity of *KY* and *BaY* zeolites is greater for *p*-xylene than for *m*-xylene (Ballat *et al.*, 1995).

At 25 °C, the adsorption processes of *p*-xylene and *m*-xylene on *Y* zeolite are not different. The adsorption capacity of α -cages is nearly the same for the two xylenes and is not changed by cation exchange with potassium or barium. Despite the fact that the external surface of faujasite is small (~ 17 m²/g), the amount of *p*-xylene adsorbed on it is significant, up to 13% of the total amount adsorbed at saturation. It is twice as great with *m*-xylene as with *p*-xylene. However, some variations of the adsorption capacity are observed according to the nature of compensation cation, temperature and pressure (Bellat *et al.*, 1997).

Gas phase adsorption of *p*-xylene and *m*-xylene on *Y* zeolite was studied by Cottier *et al.* (1997). 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 , as the last molecule of xylene is adsorbed in the α -cages, *BaY* is more selective for *m*-xylene and independent of the adsorptive mixture composition. 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 grand canonical Monte Carlo simulation program was used to model *p*-xylene and *m*-xylene adsorption of *NaY*. Biased particle insertions and deletions were implemented to allow the computation of equilibrium adsorption isotherms of such complex molecules. Single species and binary mixture isotherms at temperature of 423 K were calculated and compared to the available experimental data. Three binary mixtures corresponding to different gas phase composition were studied. The *p*-xylene and *m*-xylene selectivity predicted from the simulation is in qualitative agreement with experiment: the zeolite *NaY* preferentially adsorbs *m*-xylene isomer. A detailed analysis of the adsorbed phase structure reveals a unique adsorption site in the supercage of the zeolite located in front of the Na ion (Veronique *et al.*, 1998).

Kulprathipanja (1999) first developed the process of adsorptive separation of *m*-xylene, known as *m*-xylene Sorbex process. *m*-xylene was recovered from a mixture with other C₈ aromatic hydrocarbons including *o*-xylene by liquid adsorptive separation using sodium exchanged *Y* zeolite as the adsorbent. Performance was improved by maintaining the adsorbent in a narrow range of operating temperature and hydration. These conditions allow *m*-xylene to be recovered in a single raffinate process without costly prefraction for *o*-xylene removal.

With more advance technology, Tournier *et al.* (2000) applied two new analyzing techniques, GC and GC-C-IRMS, to the adsorption experiment. Competitive adsorption between *p*-xylene and *m*-xylene in the liquid phase on *KBaY* zeolite was studied. Both analytical techniques compare well with each other in the studied range. From the experiment, *p*-xylene selectivity depends on the composition of the liquid phase and *KBaY* is selective for *p*-xylene in the whole composition range. When the mixture is lean in *p*-xylene, the selectivity increases. However, when the mixture is rich in *p*-xylene, the selectivity is close to unity. Lastly, the Langmuir Freundlich model provides a

good fit with the experimental data. It is, thus possible to predict the adsorption equilibrium of a xylene mixture in the concentration range of 0.1% to 99.7% *p*-xylene.

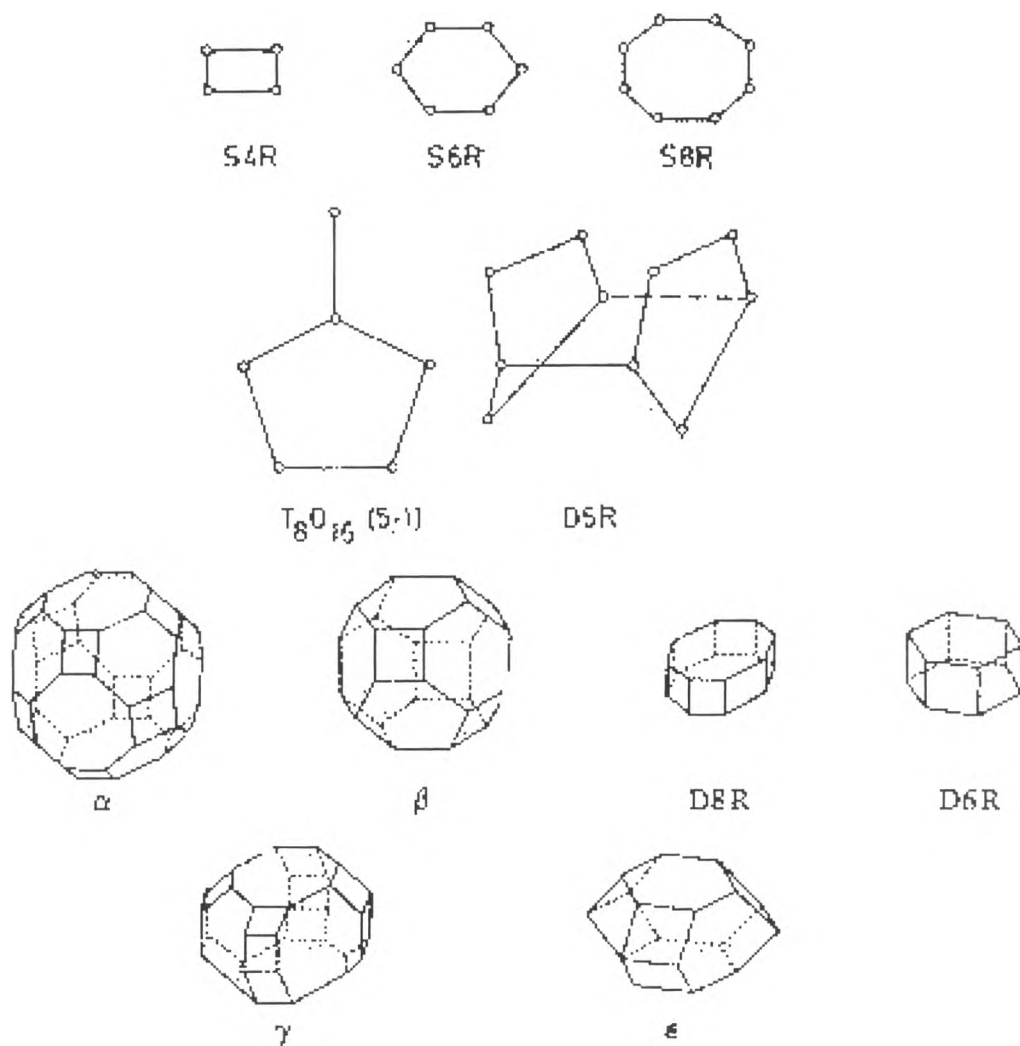


Figure 2.1 Secondary building units and commonly occurring polyhedral units in zeolite framework structures (Ruthven, 1984)

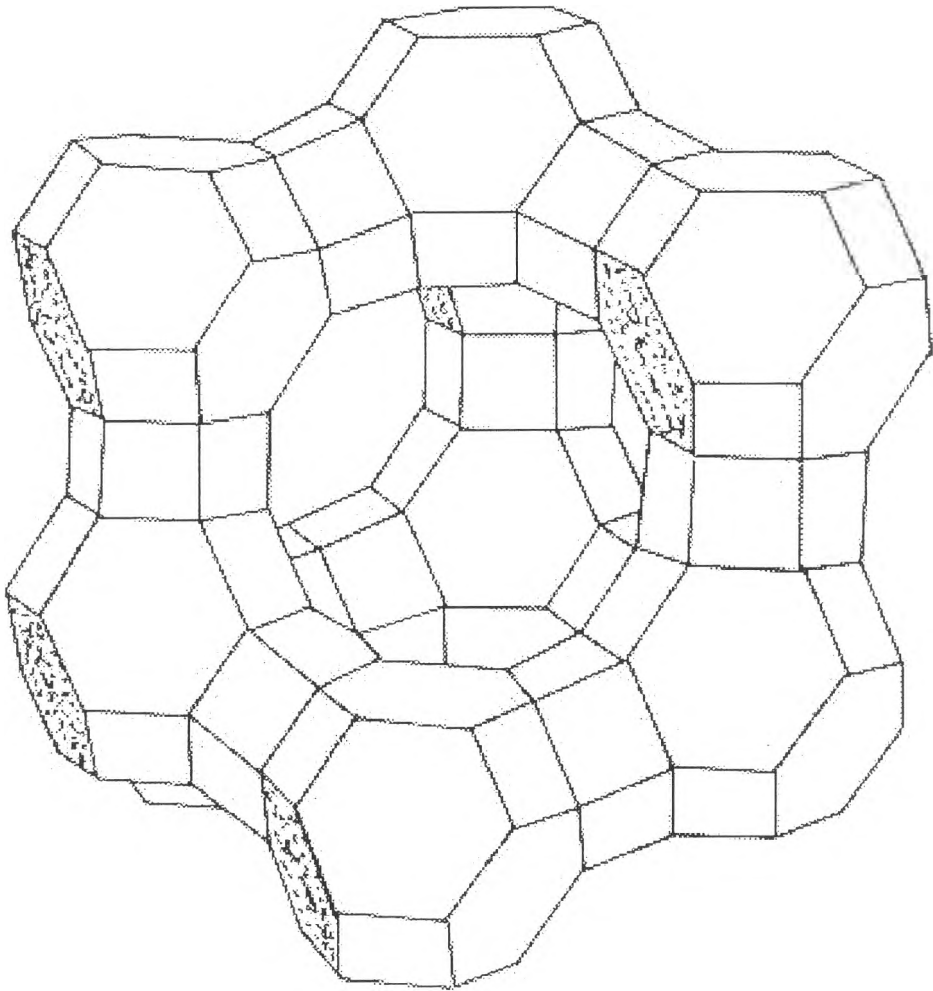


Figure 2.2 Schematic representation showing framework structures of zeolite faujasite (Ruthven, 1984)