CHAPTER II
BACKGROUND AND LITERATURE SURVEY

Background information related to this work is provided in this chapter. First, 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). After that, some related work in the separation of the C_8 aromatics are discussed. Although several types of zeolites have been and as an adsorbent in the C_8 aromatics separation, only work related to *X* and *Y* zeolites will be focused here.

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. In considering such a process, it is convenient to define a separation factor as

$$\alpha_{ab} = \frac{x_a}{x_b} \qquad (2.1)$$

where X_a and X_b are maximum %loading of component *a* and *b*, respectively. The percentage of loading is expressed in gram of the adsorbed species per gram of zeolite. 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 of 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.

Zeolites

Zeolites are porous crystalline aluminosilicates. 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 the traditional microporous adsorbents, is micropore structure.

In considering zeolite frameworks, it is convenient to regard the structures as 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 these 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 exploited means of modifying the adsorptive 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

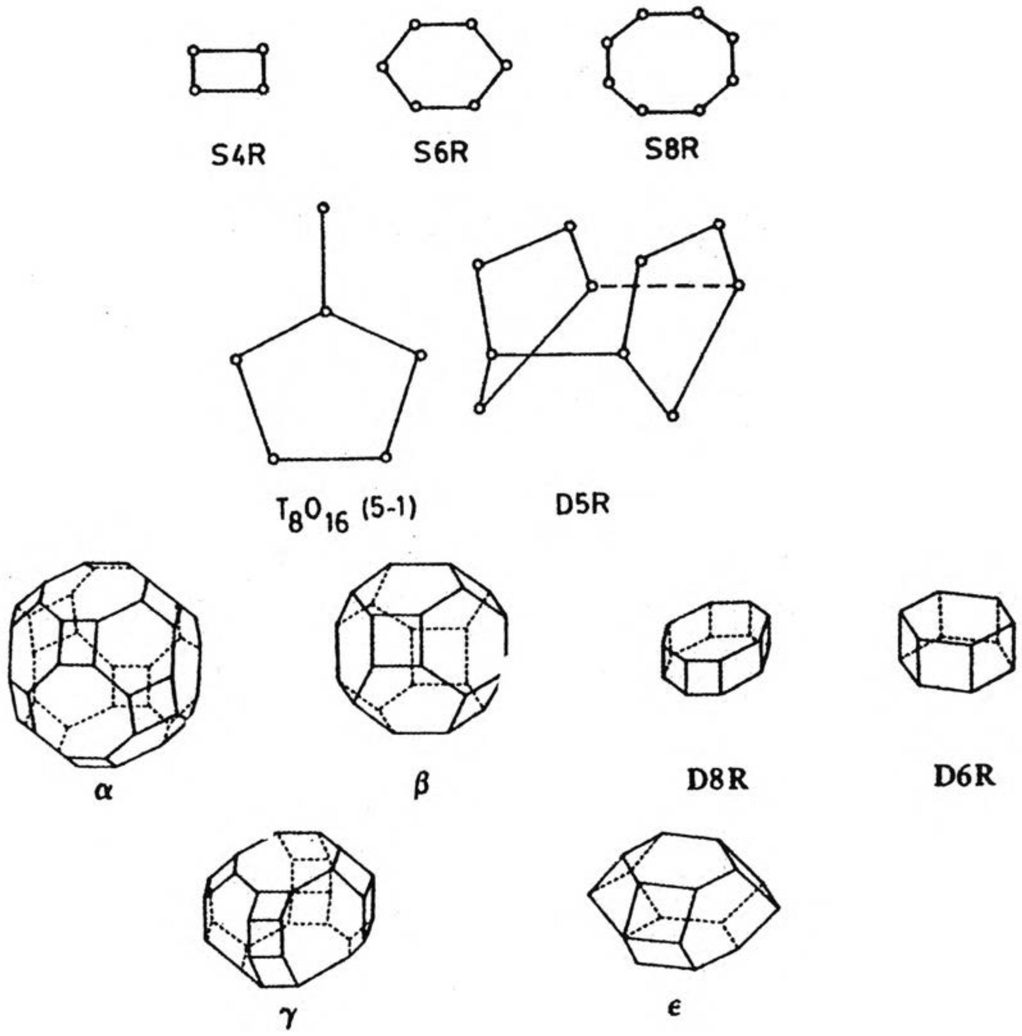

Figure 2.1 Secondary building units and commonly occuring polyhedral units in zeolite framework structures. (Ruthven, 1984)

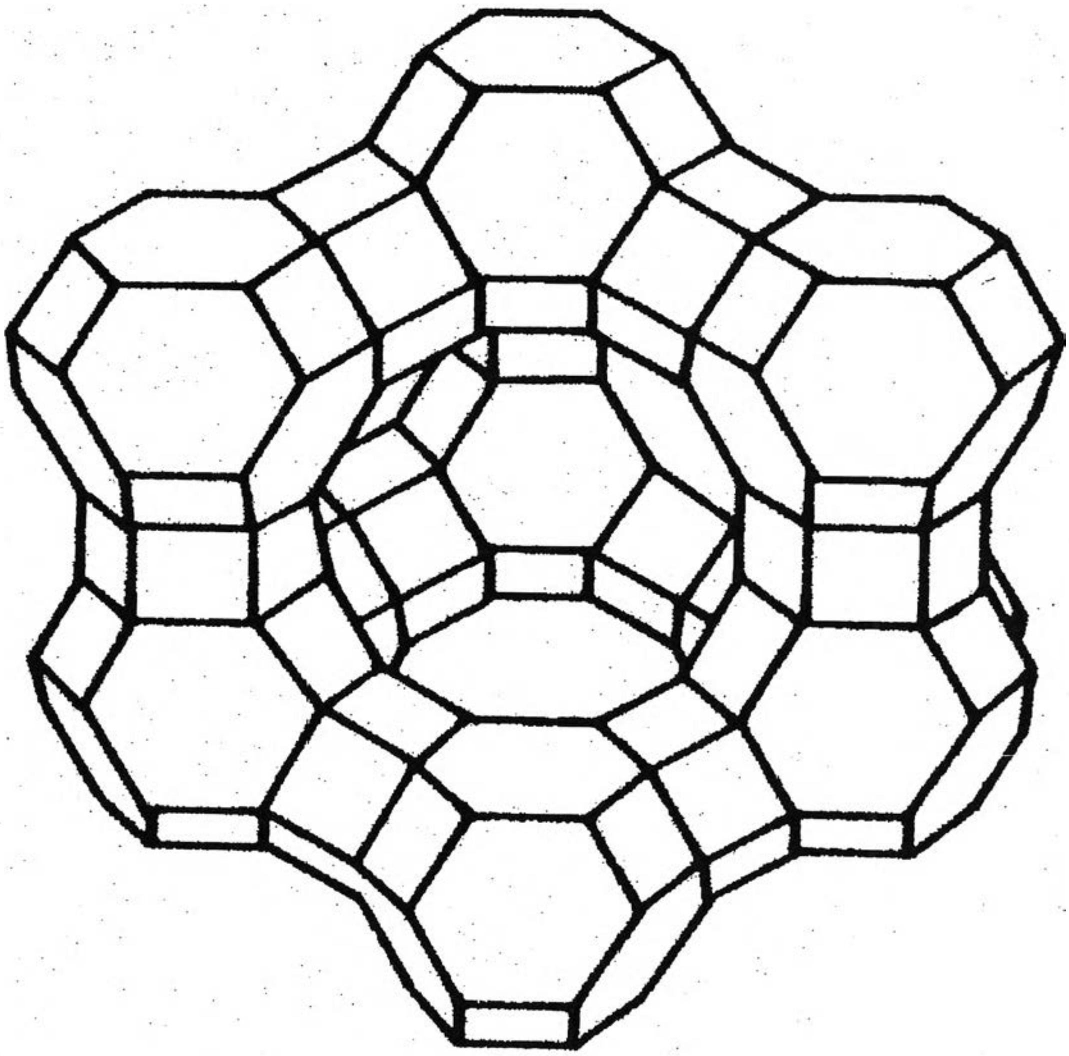

Figure 2.2 Schematic representation showing framework structures of zeolite faujasite. (Ruthven, 1984)

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 A^0. Quite 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 varies 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.

Literature Survey

ZSM-5 zeolite, which was used as the first adsorbent in the original process, was tested for the separation of *p*-xylene and ethylbenzene from the C_8 aromatic mixtures. ZSM-5 with a high SiO_2/Al_2O_3 ratio was highly selective for *p*-xylene adsorption, and the selectivity for *p*-xylene over ethylbenzene could be as high as 5.5. The total adsorption capacity of ZSM-5 was between 160 and 190 mg/g zeolite, and the competitive adsorption capacity for *p*-xylene from a typical xylene mixture was 120 mg/g zeolite. The high *p*-xylene selectivity and dependence on *p*-xylene loading are belived to be related to the unique packing of *p*-xylene in the crystalline cavities (Yan, 1989).

At 25°C, the adsorption processes of *p*-xylene and *m*-xylene on *Y* zeolites were not different. The adsorption capacities of α-cages were nearly the same for the two xylenes and not changed by cation exchange with potassium or barium. Despite the fact that the external surface of faujasite is small (~17 m^2g^{-1}), the amount of xylene adsorbed on it was significant, 13% of the total amount adsorbed at saturation. It was twice as great 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 (Bellat *et al.*, 1997).

At high temperature and low pressure, the adsorption capacities of *BaY* zeolite were greater than those of *NaY* and *KY* zolites. Thus, *BaY* zeolite showed a stronger adsorption affinity for xylenes than *NaY* and *KY* zolites. These two zeolites had a similar behavior and adsorbed a little more of *m*-xylene than *p*-xylene. At low temperature and high pressure, *KY* zeolite had 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 were greater for *p*-xylene than for *m*-xylene. The exchange of Na^+

ions by K^+ or Ba^{2+} ions leaded to a slight decrease of the maximal adsorption capacity, which was estimated at 3 molecule/α-cage at 150°C and 3.5 molecule/α-cage at 25°C for *NaY* and *KY*, respectively. After saturation of α-cages, the xylene were adsorbed on the external surface of the adsorbent (Bellat *et al.*, 1995a and 1995b).

The selectivity of *Y* zeolite depended on the filling, the composition of the mixture, and the exchangeable cation. For filling lower than 2 molecule/α-cage, *BaY* and *NaY* zeolites exhibited the same behavior toward the coadsorption of *p*-xylene and *m*-xylene and adsorbed preferentially the more abundant isomer in initial adsorptive mixture. For filling higher than 2 molecule/α-cage as the last molecules of xylenes were adsorbed in the α-cages, *BaY* zeolite was more selective for *p*-xylene whereas *NaY* zeolite was selective for *m*-xylene whatever the composition of adsorptive mixture. The adsorption selecticity for the filling lower than 2 molecule/α-cage depended only on the composition of the mixture. On the other hand, for the filling higher than 2 molecule/α-cage, exchangeable cation played an important role in the selectivity. The dependence of the composition of adsorbate on the selectivity showed a nonideal behavior of the adsorbate (Cottier *et al.*, 1997; Kitagawa *et al.*, 1996).

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 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 selectivities are of the same order of magnitude. They depend only on the nature of the compensation cation in the silica alumina ratio and the preadsorbed water amount. However, a qualitative difference arises because vapor phase adsorption studies are generally carried out at relatively low loadings whereas, in the liquid phase adsorption, the total adsorbed-phase concentration is always at or near the saturation limit (Hulme *et al.*, 1991).

M-xylene was recovered from a mixture with other C_8 aromatic hydrocarbons including *o*-xylene by liquid phase adsorptive separation using a sodium exchanged *Y* zeolite as the adsorbent. Performance was improved by maintaining the adsorbent in a narrow range of temperature and hydration. These conditions allowed the *m*-xylene to be recovered in a single raffinate process without costly prefraction for *o*-xylene removal (Kulprathipanja., 1999).

Research on the separation of xylenes by selective adsorption reported in literatures has been mainly devoted to the adsorption of xylenes in gas or liquid phases on *Y*-type zeolites. Although several commercially important adsorption separation processes, e.g., the Parex process, involve adsorption from the liquid phase, very few studied of the fundamentals of liquid-phase adsorption has been done (Furlan *et al.*, 1992).