CHAPTER II
BACKGROUND AND LITERATURE REVIEW

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:

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

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

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Most materials in this chapter were taken /summarized from Kulprathipanja and Johnson, 2001 and Ruthven, 1984

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. 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 desorption force of the desorbent (Kulprathipanja and Johnson, 2001).

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-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-dimensional hydrocarbon network attached 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 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 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 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 compound with their crystal structures containing large pores and voids. Effective pore sizes in microporous solids range from 0.3 nm to over 1 nm, 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 tetrahedral, 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 polyhedral, which consists of several SiO_4 and AlO_4 tetrahedral, are shown schematically in Figure 2.1 In the diagrams, each vertex represents the location of a *Si* of *Al* atom while the lines represent, approximately, the diameters of the oxygen atoms ions, which are very much larger than the tetrahedral *Si* or *Al* atoms.

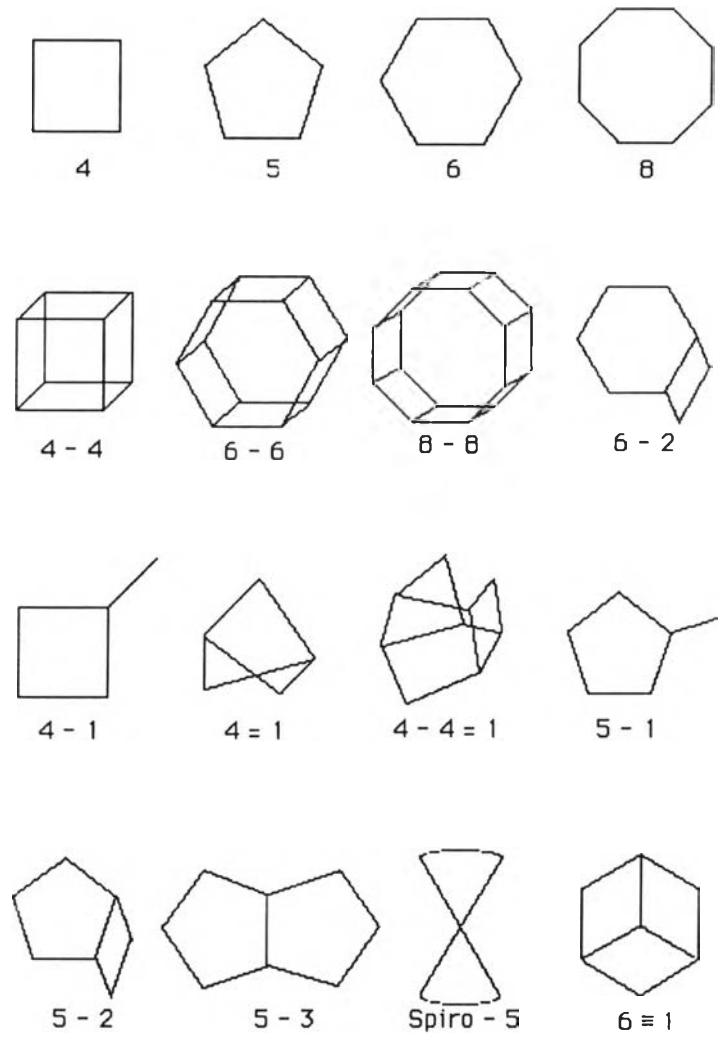

Figure 2.1 Secondary building units and commonly occurring polyhedral units in zeolites framework structure (http://chemmac1.usc.edu/bruno/zeodat/Intro.html).

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 silicalite zeolite is an aluminum-free form of ZSM-5. The structure base on the double five-ring unit (D5R). The structure of a characteristic layer of silicalite is shown schematically in Figure 2.2. By stacking such layers in different sequences a variety of related structures may be obtained. The channel

systems of the silicalite are sketched in Figure 2.3. This zeolite has a two-dimensional pore structure consisting of straight channels (pore size, 0.51x 0.54 nm) with intersecting sinusoidal channels (pore size, 0.54 x 0.56 nm), composed of 10-membered oxygen rings. Each unit cell is constructed from four segments of linear channel, four segments of sinusoidal channel, and four channel intersections (Olson *et al.*, 1981).

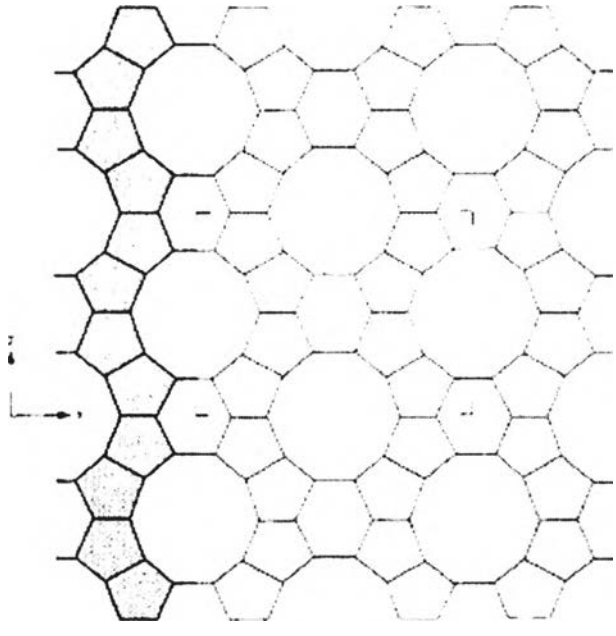

Figure 2.2 Characteristic layer of silicalite (Olson *et al.*, 1981).

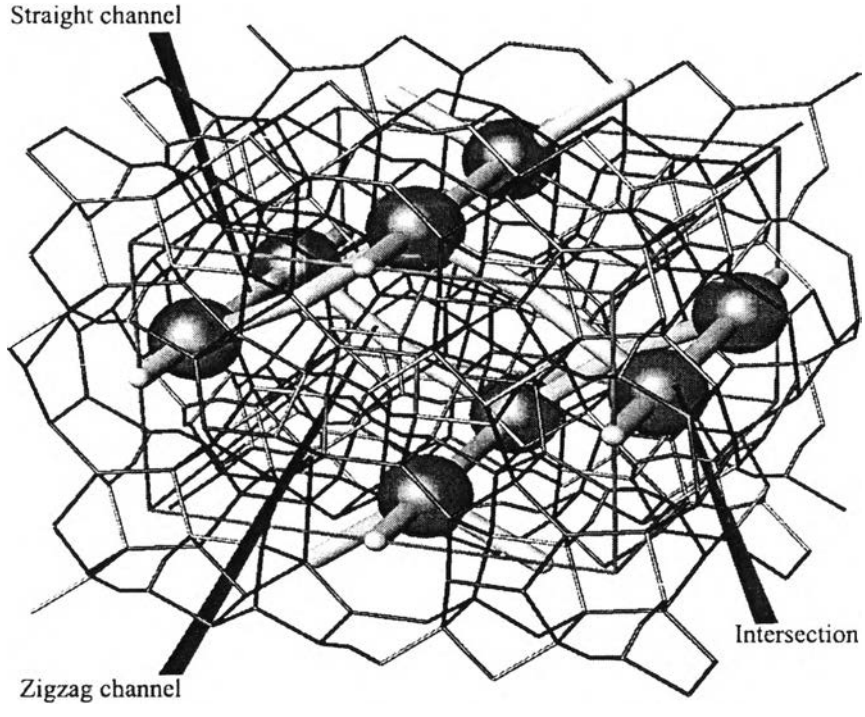

Figure 2.3 3-Dimention of the pore structure of silicalite.

2.2 Literature Review

Liquid phase adsorption mechanisms of n-paraffin and n-olefin by silicalite are highly complex. The difference in pore structure of the silicalite is one of many factors that play a major role of the adsorption mechanism. For the regular three-dimensional silicalite-I pore structure, it is instructive to express the preferential location in terms of molecules per unit cell (m/uc).

The critical diameters of C_1-C_{20} normal alkanes and alkenes are all about 0.52 nm which are less than the pore diameter of silicalite (about 0.54 nm). Therefore, the adsorption equilibrium capacity of n-paraffin and n-olefin on the silicalite zeolite was expected to depend on molecular chain length than the molecular kinetic diameter, and to decrease linearly as molecular chain length increase.

Richards and Rees (1987) have studied the details of adsorption/desorption isotherms for ethane, propane, butane, and hexane on H-ZSM-5 (Si/Al = 132) by using gravimetric balance. They proposed the sorption model that attempts to explain the variation of isosteric heats of sorption with coverage observed for n-alkanes sorbed in silicalite. The results show that methane and ethane, which have smaller molecular lengths than that of either the straight or the sinusoidal channel, can locate one molecule in a straight channel as well as in a sinusoidal channel. However, for methane and ethane about 8 m/uc can be positioned in channel segment without major interaction between sorbate-sorbate molecules; therefore, the isosteric heats of adsorption would be constant. On the other hand, butane is impossible to locate any of the molecules into the channel segment without invasion into the intersection. Sine sinusoidal channel is longer than straight channel; hence, assumptions preferentially locate molecules in the sinusoidal channel segment for sorbate molecule less than 4 m/uc. For higher 4 m/uc, the sorbate-sorbate interaction could occur, therefore enhancing isosteric heat of adsorption. This increase in the isosteric heat of adsorption with loading can be attributed to sorbate-sorbate interaction.

Zhu *et al.* (1998) used TEOM technique to measure adsorption for methane, ethane, propane, n-butane, and i-butane. Single component adsorption isotherms were reported in the temperature range of 303 to 473 K and pressure up to 500 kPa. They found that the isotherms of the four n-alkane exhibit a type-I adsorption isotherm, and as the molecular length increases, the adsorption capacity decreases. Moreover, the increasing of the temperature decreases the saturation capacity.

Sun *et al.* (1996) have studied adsorption isotherms of n-pentane to n-decane on silicalite crystals by gravimetrical technique at the temperature ranging from 30 to 150 ^{o}C and at pressure up to 1333 Pa. As expected, they found that the adsorption capacity decreases with increasing carbon number. In addition, the saturation capacity decreases substantially from heptane to octane instead of dropping linearity with the molecular length. They suggested that n-hexane to n-octane fill up the straight channels but the packing in sinusoidal channels is less dense due to the highest CH_2 packing efficiency is also reached for heptane. It implies that alkanes with carbon number less than seven can efficiently occupy all

the pores of silicalite. For octane and higher alkanes, because of the extra CH_2 groups, inefficiency in packing results in a lower CH_2 density in the pore system.

To understand the unusual behavior for n-paraffin packing in the silicalite, De Meyer *et al.* (2003) have studied the liquid-phase adsorption of C_5-C_{22} linear alkanes on ZSM-5 using a batch adsorption technique and compared the adsorption experiment result with the simulation result. The configurational-bias grand canonical Monte Carlo (CB-GCMC) simulations were used in this study to investigate the equilibrium capacity and mechanisms of packing in liquid-phase adsorption in the pore system of silicalite. The obtained data provides insight into the dependence of saturation capacity on alkane chain length and the geometry of the pore system and the underlying adsorption mechanisms.

C_5 and C_6 have lengths less than the distance between intersections and void sitting in the intersections. C_7 crosses the intersection and spans into adjacent channel space, which leads to a lower number of molecules adsorbed per unit cell. C_8 and longer alkanes sit in a different way in the pore system. These molecules place the center of their chain near the intersections, with their head and tail pointing into the channels. This results in a completely different, less efficient type of packing as molecules such as C_8 nearly does not bend and cross at all in the intersections. With increasing chain length, the probability of bending from one channel type to another and of crossing of alkane molecules in the intersections becomes larger. Although the number of molecular packing per unit cell in the pore of silicalite decreases rapidly between C_7-C_8, the number of adsorbed $-CH_x$ groups per unit cell increases from C_8 on until it reaches a plateau for C_{14}-C_{22} of 53-54. The observation that the number of adsorbed $-CH_x$ groups per unit cell remains constant from C_{14} on indicates that the pore system of ZSM-5 is completely and very densely packed (De Meyer *et al.*, 1996).

Many experimental techniques have been developed to study diffusivity of n-paraffin in silicalite. These include concentration pulse chromatography (CPC), zero length column (ZLC), pulsed field gradient nuclear magnetic resonance (PFG-NMR), quasi-elastic neutron scattering (QENS), frequency response (FR), and membrane techniques. Unfortunately, for many adsorbate/adsorbent systems, the

micropore diffusion coefficients determined from various techniques have been found to differ by up to 4 orders of magnitude (Hufton and Danner, 1993).

Talu *et al.* (1998) used a single-crystal membrane (SCM) technique to measure micropore diffusivities of C_1 to C_{10} normal alkanes at 30, 50 and 70 °C. Normally the diffusivity is expected to decrease with the increase in the chain length but the unexpected increase in diffusivity from hexane to heptane to octane was observed. They attributed these unusual phenomena to density and location of the molecule in the pore system.

In the C_1-C_{10} range, hexane has the lowest diffusivity since its length almost exactly matches the length of the sinusoidal channels. There are evidences that indicate the freezing of hexane in the sinusoidal channels and the diffusion is retarded if the hexane is frozen in the sinusoidal channels, which acts like a bottleneck. The longer alkanes do not fit in a single channel. Although heptane and octane molecules are long enough to occupy two straight segments in sequence, such the configuration does not contribute to diffusion flux. Hence, they must occupy both types of channels simultaneously. The leading CH_2 groups in a chain that may be in a straight channel can act like a guide for the remainder of the chain in a sinusoidal channel for a smoother move between the two channels. This scenario coupled with the lower CH_2 density in the system explains the substantial increase in diffusivity from heptane to octane (Talu *et al.*, 1998).

The adsorption of methane, ethane, ethylene, and carbon dioxide on silicalite and the thermodynamics of adsorption have been investigated under similar conditions using a gravimetric adsorption apparatus (Choudhary and Mayadevi, 1996). The order for the adsorption of the different adsorbates on silicalite-I is $CH_4 < CO_2 < C_2H_4 \lesssim C_2H_6$. The Dubinin-Polanyi equation was found to fit the isotherm data for the adsorption of methane (305 K) and ethane (305-413 K); the Freundlich equation fits the adsorption data for methane (353 K), ethane (453 K), and carbon dioxide (353 K); and the adsorption of ethylene (305, 353 K) and carbon dioxide (305 K) follows the Langmuir isotherm model. The isosteric heat of adsorption for the adsorption of these gases on silicalite-I lies between 18 and 32 $kJ \cdot mol^{-1}$, with ethane having the highest value. The heat of sorption is affected

mildly by the surface coverage for all the gases but methane. The heat of adsorption of methane decreases with an increase in its loading. Analysis of the entropy of adsorption reveals that ethane (at an adsorbate loading of <0.8 mmol · g^{-1}), methane, ethylene, and carbon dioxide (at all adsorbate loadings studied) are supermobile on the silicalite surface. The mobility of adsorbed methane increases, and that of the other adsorbates decreases with increasing the adsorbate loading.

Denayer *et al.* (2003) studied the adsorption of binary mixtures of n-alkanes with chain lengths up to C_{22} from the liquid phase on ZSM-5 zeolite and reported the unexpected selectivities depending on subtle differences in the number of carbon atoms. Selective adsorption of the short alkane compound was observed with C_{14}/C_{15} and C_{15}/C_{16}. Selective adsorption of the heaviest molecule occurred with C_5/C_6, C_6/C_{14}, C_8/C_9, C_8/C_{12}, C_9/C_{11}, C_9/C_{12}, and C_9/C_{13}. Azeotropic behavior observed with C_5/C_7, C_6/C_7, C_6/C_8, C_7/C_8, C_6/C_{10}, C_{13}/C_{14}, C_{17}/C_{18}, and C_{20}/C_{22}. Azeotropic behavior was identified by a reversal of selectivity, at a specific composition where adsorbate and liquid have identical composition. Pronounced adsorption selectivity for the short chain was observed with C_{14}/C_{15} and C_{15}/C_{16}. They ascribed the favorable adsorption of C_{14} and C_{15} to molecular chain length matching with characteristic dimensions of the pore system. The chain length of C_{14} corresponds to the length of two sinusoidal channel segments and an intersection, but also fits into two linear-channel segments and two intersections. The length of a C_{15} molecule exceeds the dimensions of two sinusoidal-channel segments and an intersection but still fits into two linear-channel segments and two intersections. A stretched C_{16} molecule does not fit into either of these combinations, and thus always blocks an additional intersection compared to C_{15} or C_{14}. A similar reasoning in terms of the matching of alkyl-chain lengths and pore-segment lengths explains the behavior of mixtures containing C_5 or C_6. These molecules fit neatly into a sinusoidal channel segment, whereas longer alkanes block intersections. Admixing C_5 or C_6 with a longer alkane fitting less well with a characteristic pore length gives rise to azeotrope behavior (C_5/C_7, C_6/C_7, C_6/C_8, C_6/C_{10}). These mixtures fill the pores only partially. At low concentration of the long chain, it is preferentially adsorbed because of its higher adsorption enthalpy. From a critical concentration of these long chains on, C_5 or C_6 adsorption is preferred because of their better fitting

with the sinusoidal channels. This reversal of selectivity, depending on concentration, explains the azeotropic behavior.

A combination of experimental and computational studies of adsorption from liquid-phase binary mixtures of linear alkanes in the zeolite silicalite was investigated by Chempath *et al.* (2004). From the experimental results, the mixture of C6/C7 shows selectivity for the shorter alkane over the whole range of compositions. The mixtures of C5/C6,C5/C7,C6/C8, and C6/C10 show selectivity for shorter alkanes over some concentration range and for the longer one over another range. They, thus, exhibited azeotropy and a reversal in selectivity depending on composition. The mixtures of C7/C8, C8/C9, and C8/C12 show selectivity for the longer alkane over the whole concentration range. Excellent agreement between the experiments and CB-GCMC simulations was observed for all cases. A site-based analysis of the adsorption data also revealed that alkanes do not distribute uniformly among the adsorption sites, shorter alkanes are pushed into the less favorable zigzag channels while the longer alkanes occupy the straight channels. Both the intramolecular energies and the zeolite-sorbate energies are lower for alkanes adsorbed in straight channels compared to those in zigzag channels.

Alkane pure components and alkane/alkene binary mixtures adsorption isotherms was computed by grand canonical Monte Carlo simulations (Pascual *et al.* 2004). Simulated results was in good agreement with available experimental data, and it shown that the difference between adsorption heats is responsible for the observed selectivity at low coverage and that at high coverage, selectivity is driven by entropy effects.