Chapter II

Theory

Molecular sieves vs. zeolites

In 1932 McBain proposed the term "molecular sieve" to describe a class of materials that exhibited selective adsorption properties. He proposed that for a material to be a molecular sieve, it must separate components of a mixture on the basis of molecular size and shape differences. Two classes of molecular sieves were known when McBain put forth his definition: the zeolites and certain microporous charcoals. The list now includes the silicates, the metallosilicates, metalloaluminates, the $AlPO_4$'s, and silico- and metalloaluminophosphates, as well as the zeolites. The different classes of molecular sieve materials are listed in Figure 2.1. All are molecular sieves, as their regular framework structures will separate components of a mixture on the basis of size and shape.
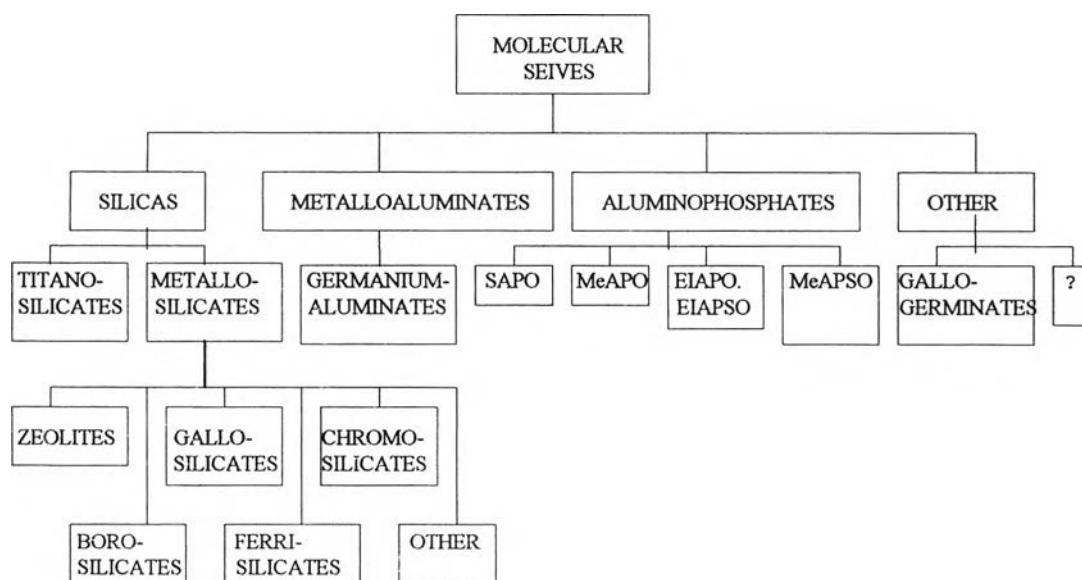

Figure 2.1 Classification of molecular sieve materials [9].

2.1 Molecular sieves

A molecular sieve framework is based on an extensive three-dimensional network of oxygen ions containing generally tetrahedral type sites. In addition to the Si^{+4} and Al^{+3} that compositionally define the zeolite molecular sieves, other cations also can occupy these sites. These cations need not be isoelectronic with Si^{+4} or Al^{+3}, but must have the ability to occupy framework sites. Cations presently known to occupy these sites within molecular sieve structures are listed in Table 2.1. The zeolite molecular sieves display a net negative framework charge; however, a molecular sieve framework need not display any charge. Molecular sieves containing only Si^{+4} in the tetrahedral sites known as silicalite have a neutral framework and exhibit a high degree of hydrophobicity and no ion exchange capacity [9].

Table 2.1 Cations that may form molecular sieve framework structures and the metal oxide charge possible [9].

	M
$(M^{+2}O_2)^{-2}$	Be, Mg, Zn, Co, Fe, Mn
$(M^{+3}O_2)^{-1}$	Al, B, Ga, Fe, Cr
$(M^{+4}O_2)^{0}$	Si, Ge, Mn, Ti
$(M^{+5}O_2)^{+1}$	P

2.2 Zeolites

The zeolite is a crystalline aluminosilicate with a framework based on an extensive three-dimensional network of oxygen ions. Situated within the tetrahedral sites formed by the oxygen can be either a Si^{+4} or an Al^{+3} ion. The AlO_2^- tetrahedra in the structure determine the framework charge. This is balanced by cations that occupy nonframework positions. The chemical formula for a zeolite is written as:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$
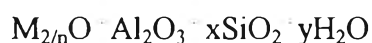
M represents the exchangeable cations, generally from the group I or II ions, although other metal, nonmetal, and organic cations may also be used to balance the framework charge, and n represents the cation valence. These cations are present either during synthesis or through post-synthesis ion exchange. The value of x is equal to or greater than 2 because Al^{+3} does not occupy adjacent tetrahedral sites. The crystalline framework structure contains voids and channels of discrete size, unlike the microporous charcoal molecular sieves, a characteristic that separates them from the amorphous carbon molecular sieves. The pore or channel openings range from 3 Å to 8 Å, depending on the structure. Water molecules present are located in these channels and cavities, as are the cations that neutralize the negative charge created by the presence of the AlO_2^- tetrahedra in the structure. Typical cations include: the alkaline (Na^+, K^+, Rb^+, Cs^+) and alkaline earth (Mg^{+2}, Ca^{+2}) cations, NH_4^+, H_3O^+ (H^+), TMA^+ (tetramethylammonium) and other nitrogen-containing organic cations, and the rare-earth and noble metal ions [9].

2.2.1 Zeolite structure

There are two types of structures: one provides an internal pore system comprising interconnected cage-like voids; the second provides a system of uniform channels which are one-dimensional and in others intersect with similar channels to produce two- or three-dimensional channel systems. The preferred type has two- or three-dimensional channel systems to provide rapid intracrystalline diffusion in adsorption and catalytic applications. In most zeolite structures, the primary structural units, tetrahedra, are assembled into secondary building units, which may be simple polyhedral such as cubes, hexagonal prisms or truncated octahedral. The final framework structure consists of assemblages of the secondary units [1].

2.2.2 Pore size and dimension

The interest in a particular zeolite is based on its ability to selectively adsorb one component of a mixture over another. It is important to identify the size of the pore opening necessary to achieve the desired selectivity. For example, zeolite types

A and X differ in their adsorption properties for organic molecules. In a process that requires the separation of linear from branched paraffins, calcium exchanged zeolite type A would be the preferred zeolite. The size of the pore opening of zeolite type A is 4.8 Å resulting in selective adsorption of the small unbranched hydrocarbons. The branched hydrocarbons are too large to readily enter the pores of this structure. Zeolite type X have large pore channel system (7.6 Å) which would not be selective in this process, as it will adsorb both the linear and the branched hydrocarbons [9].

All zeolites that are significant for catalytic and adsorbent applications can be classified by the number of T atoms, where T = Si or Al, that define the pore opening. There are only three pore openings known in the aluminosilicate zeolite system that are of practical interest for catalytic applications; they are descriptively referred to as the 8, 10 and 12 ring openings. These pore openings may also be referred to as small (8-member ring), medium (10-member ring) and large (12-member ring) pore zeolites. The simplified classification system based on the different number of T atoms defining the opening for three representative zeolites: erionite, ZSM-5 and type Y zeolite are shown in Figure 2.2 . Some zeolites of known structure are listed in Table 2.2-2.4.
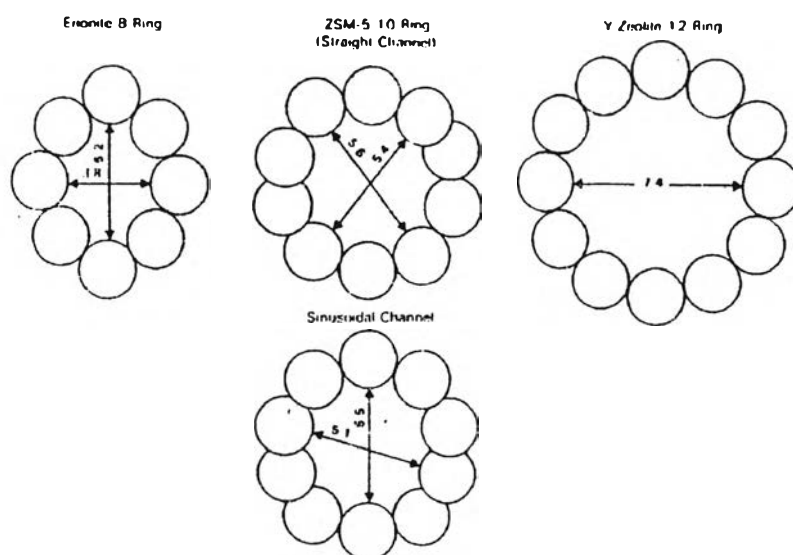
Figure 2.2 Examples of the three types of pore openings in the zeolite molecular sieves. Erionite contains an 8 ring pore opening; ZSM-5, two 10 ring systems differing in the shape of the opening; type Y zeolite, a 12 ring pore system [9].

Table 2.2 Known zeolite structures listed by pore opening, as defined as the number of T units that shape the channel [9].

12 RING	10 RING	8 RING
Faujasite (Type X, Y)	ZSM-5 (Silicalite)	Type A, ZK-5
Mordenite	ZSM-11	Bikitaite
Cancrinite	Dachiardite	Brewsterite
Gmelinite	Epistilbite	Chabazite
Type L	Ferrierite	TMA-E (AB)
Mazzite	Laumontite	Edingtonite
Offretite	Stilbite	Erionite
Omega	ZSM-23	Gismondine
ZSM-12	Theta-1 (ZSM-22)	Heulandite
Beta	Eu-1 (ZSM-50)	Levyne
	ZSM-48 (EU-2)	Merlinoite
		Natrolite
		Phillipsite
		Paulingite
		Rho
		Thomsonite
		Yugawaralite

Table 2.3 Pore structure of zeolite [10].

Type code	Name	Pore system	Pore dimensions (Å)
BIK	Bikitaite	8	3.2 X 4.9
BRE	Brewsterite	8	2.3 X 5.0
CHA	Chabasite	8	3.6 X 3.7
DAC	Dachiardite	10; 8	3.7 X 6.7; 3.6 X 4.8
EAB	TMA-E(AB)	8	3.7 X 4.8
EDI	Edingtonite	8	3.5 X 3.9
EPI	Epistilbite	10; 8	3.2 X 5.3; 3.7 X 4.4
ERI	Erionite	8	3.6 X 5.2
FAU	Faujasite(X,Y)	12	7.4
FER	Ferrierite	10; 8	4.3 X 5.5; 3.4 X 4.8
GME	Gmelinite	12; 8	7.0; 3.6 X 3.9
HEU	Heulandite	10; 8	4.0 X 5.5; 4.4 X 7.2
KFI	ZK-5	8	3.9
LTA	Linde Type A	8	4.1
LTL	Linde Type L	12	7.1
MAZ	Mazzite	12	7.4
MEL	ZSM-11	10	5.1 X 5.5
MFI	ZSM-5	10	5.4 X 5.6; 5.1 X 5.5
MOR	Mordenite	12; 8	6.7 X 7.0; 2.9 X 5.7
OFF	Offretite	12; 8	6.4; 3.6 X 5.2
PAU	Paulingite	8	3.9
RHO	Rho	8	3.9 X 5.1
STI	Stilbite	10; 8	4.1 X 6.2; 2.7 X 5.7

Table 2.4 Some dimensional parameters of common zeolites [3].

Zeolite	Restricting windows (number of O atoms)	Effective window size ^{a} (Å)	Void volume ^{b}	Other dimensions
Zeolite A	6	2.3	0.47	β cage diameter : 6.6 Å
	8	4.5		α cage diameter : 11.4 Å
Zeolite X	6	2.3	0.53	α cage diameter : 11.8 Å
	12	7.8		
Zeolite L	12	7.1	0.28	
Heulandite	8	4.0 x 5.5	0.35	} Interconnected
	10	4.4 x 7.2		
Phillipsite	8	4.2 x 4.4	0.30	} Interconnected
	8	2.8 x 4.8		
	8	3.3		
Mordenite	12	6.7 x 7.0	0.26	} Interconnected
	8	2.9 x 5.7		
Chabazite	8	3.6 x 3.7	0.48	
Analcime	6	2.6	0.18	
Zeolite ZSM-5	10	5.6 x 5.4	0.32	

^{a} May act be the crystallographic measurements.
^{b} Expressed as cm ^{3} liquid H_2O/cm^3 crystal.

8-member ring systems

The shape of the 8-member ring varies from circular to puckered and elliptical. The dimension of the pore opening also varies accordingly. For example, Linde A and ZK-5 have circular openings, while erionite and chabazite have puckered and elliptical pore openings. The effective pore size depends on the interaction of the intramolecular and the interatomic forces between the host structure and the diffusing molecules. The application of this group uses for sorbing straight chain molecules, such as n-paraffins and olefins and primary alcohol [10].

10-member ring systems

These are known as medium pore zeolites which their framework structures contain 5-membered oxygen rings. The 10-member ring zeolites are more siliceous thus, these groups may be considered as "silicates". The shape and size of the 10-member ring zeolites varies from nearly circular to elliptical to odd shapes such as teardrop. Among the zeolites in this group, only ZSM-5 and ZSM-11 have bi-directional intersecting channels. The others have nonintersecting unidirectional

channels [10]. Figure 2.3 shows the projections of the main channels for some of the zeolites.

ZSM-5 0.54 × 0.56   ZSM-11 0.51 × 0.55   ZSM-48 0.53 × 0.56

ZSM-23 0.45 × 0.56   ZSM-12 0.57 × 0.61
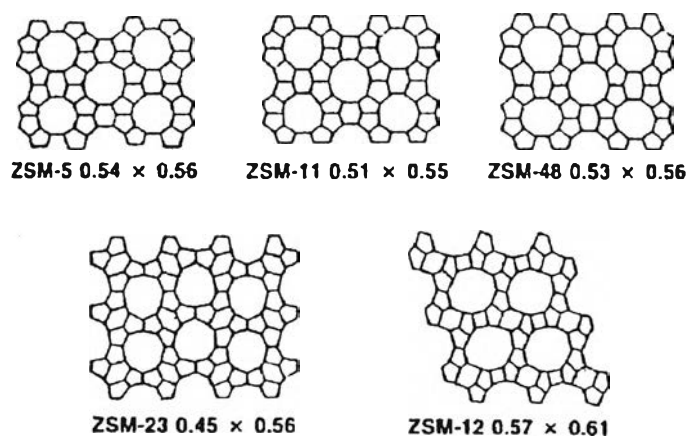
Figure 2.3 Projections of ZSM-5, -11, -12, -23 and -48 structures [10].

12-member ring systems

Zeolites in Table 2.2 are classified in terms of their largest pore opening. Faujasite (Type X, Y) and mazzite are 12-member ring openings. Gmelinite, mordenite and offretite are 12- and 8-member ring opening as shown in Table 2.3 and 2.4. Large pore zeolites deactivate much more rapidly than medium or small pores in acid catalyzed reactions. Some of these zeolites show interesting catalytic properties in cracking reactions. For example, cracking of paraffins over offretite was found to yield more low-molecular-weight cracked products than that produced from medium pore zeolites [9 , 10].

2.2.3 Zeolite properties

Actually, three main properties of zeolites are adsorption, catalysis and ion exchange. The following context will be concentrated on only adsorption which involves closely with the separation processes.

Adsorption

Several types of microporous solids are used as adsorbents for the separation of vapor or liquid mixtures, the distribution of pore diameters does not enable separations based on the molecular sieve effect. The most important molecular sieve effects are shown by crystalline zeolites.

Zeolites are high capacity and selective adsorbents. They adsorb molecules with a selectivity that is not found in other solid adsorbents. The separation may be based on the molecular sieve effects or may involve the preferential or selective adsorption of one molecular species over another. These separations are governed by several factors. The basic framework structure, or topology, of the zeolite determines the pore size and the void volume. The exchange cations, in terms of their specific location in the structure, their population density, their charge and size, affect the molecular sieve behavior and adsorption selectivity of the zeolite as shown in Figure 2.4 [1].
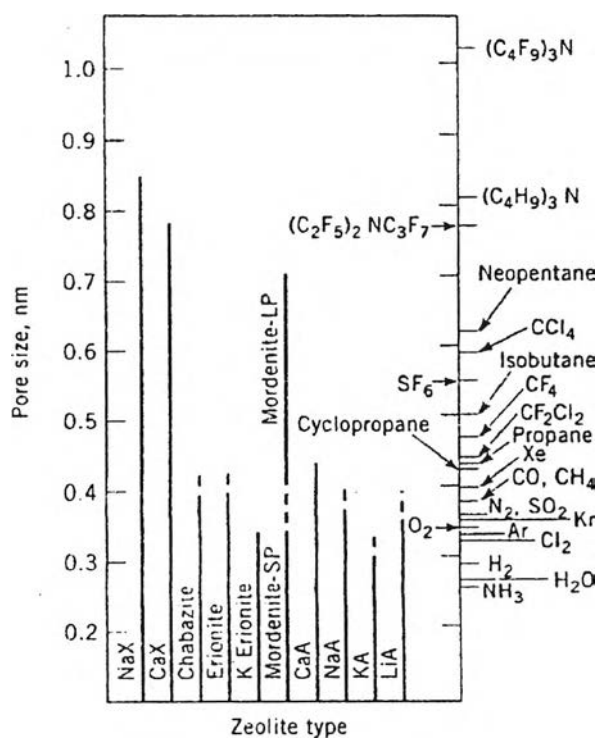
Figure 2.4 Molecular dimension and zeolite pore size [1].

Force of adsorption

Adsorption may be classified as chemisorption or physical adsorption, depending on the nature of the surfaces. In chemisorption there is significant electron transfer, equivalent to the formation of a chemical bond between the sorbate and the solid surface, and monolayer formation whereas physical adsorption the forces are mainly van der Waals interactions, involving multilayer formation [11]. Table 2.5 shows the difference in the general features of physical and chemisorption systems [12].

Heterogeneous catalysis generally involves chemisorption of the reactants, but most applications of adsorption in separation and purification processes depend on physical adsorption.

Table 2.5 Parameters of physical adsorption and chemisorption [12].

Parameter	Physical adsorption	Chemisorption
heat of adsorption (ΔH)	low, > 1–5 times latent heat of evaporation	high, > 1–5 times latent heat of evaporation
specificity	nonspecific	highly specific
nature of adsorbed phase	monolayer or multilayer, no dissociation of adsorbed species	monolayer only may involve dissociation
temperature range	only significant at relatively low temperatures	possible over a wide range of temperature
forces of adsorption	no electron transfer, although polarization of sorbate may occur	electron transfer leading to bond formation between sorbate and surface
reversibility	rapid, nonactivated, reversible	activated, may be slow and irreversible

Selectivity

Selectivity in a physical adsorption system may depend on differences in either equilibrium or kinetics, but the great majority of adsorption separation processes depend on equilibrium-based selectivity. Significant kinetic selectivity is in general restricted to molecular sieve adsorbents, e.g., carbon molecular sieve,

zeolites. In these materials the pore size is of molecular dimensions, so that diffusion is sterically restricted. In this regime small differences in the size or shape of the diffusing molecule can lead to very large differences in diffusivity. In the extreme limit one species may be completely excluded from the micropores, thus giving a highly selective molecular sieve separation. A degree of control over the kinetic selectivity of molecular sieve adsorbents can be achieved by controlled adjustment of the pore size whereas the control of equilibrium selectivity is generally achieved by adjusting the balance between electrostatic and van der Waals forces [12].

Hydrophilic and hydrophobic surfaces

Polar adsorbents such as most zeolite, silica gel, or activated alumina adsorb water more strongly than they adsorb organic species and they are commonly called hydrophilic. In contrast, nonpolar surface where there is no electrostatic interaction water is held only weakly and is easily displaced by organics. Such adsorbents, which are the only practical choice for adsorption of organics from aqueous solutions, are termed hydrophobic. Because of the good property as a selective adsorbent for nonpolar molecules, silicalite is selected. A sample of the common adsorbents is shown in Table 2.6.

Table 2.6 Common adsorbents [12].

Adsorbents		
Surface polarity	Pore size distribution	
	Narrow	Broad
polar (hydrophilic)	zeolites (Al rich)	activated alumina silica gel
nonpolar (hydrophobic)	carbon molecular sieves silicalite	activated carbon

The most common hydrophobic adsorbents are activated carbon and silicalite. It seems clear that the channel structure of silicalite must inhibit the hydrogen bonding between occluded water molecules, thus enhancing the hydrophobic nature

of the adsorbent. Silicalite has some potential as selective adsorbent for the separation of alcohols and other organics from dilute aqueous solutions [6,7].

2.2.4 Applications of zeolites

The applications of zeolites are extensive. They can be divided into categories based on the properties of the zeolites that is being utilized:

1. Separation according to molecular size and shape.

2. Catalysis.

3. Ion exchange.

Separations according to molecular size and shape are accomplished by selection of the dimensions of the zeolite so that one type of molecule can enter the pore whereas anothers cannot. Some commercially available molecular sieve products and related materials for separation processes are shown in Table 2.7, classified according to the basic zeolite structure types. Figure 2.5 shows the classification of adsorptive separations.

As can be seen from Figure 2.5, separation of p-, m- and o-xylenes is one of the liquid-phase separations. UOP have pioneered the use of synthetic zeolites to fractionate mixtures of liquids. They have developed a series of applications, generically described as "Sorbex" processes, as shown in Table 2.8 [3].

The manufacture of mixed xylenes and subsequent production of high purity p-xylene and o-xylene involves a series of steps in which the mixed xylenes are produced from the relevant petroleum fraction, pure p-xylene and/or o-xylene are separated from the mixed xylenes stream, and the p-xylene (and perhaps o-xylene) depleted stream is reisomerized to an equilibrium mixture of xylenes.

Table 2.7 Commercial molecular sieve products [1].

Zeolite type	Designation	Cation	Effective pore diameter, Å	Unit cell parameter,[c] Å
A, KA	3A[d,e]	K	3	UOP
	Zeolum A-3[d,e]			TOSOH
	Sylosiv A3[c]			Grace Davison
A, NaA	4A[d,e]	Na	4	UOP
	Zeolum A-4[d,e]			TOSOH
	Valfor G100			PQ
	Sylosiv A4[e]			Grace Davison
A, CaA	5A[d,e]	Ca	5	UOP
	Zeolum A-5[d,e]			TOSOH
X, NaX	13X[d]	Na	10	UOP
	Zeolum F-9[d,e]			TOSOH
	Sylosiv A10[e]			Grace Davison
Y, NaY	LZY-54[d]	Na	10	UOP (5.0); $a_0 = 24.68$
	HSZ-320NAA[d,e]			TOSOH (5.5); $a_0 = 24.64$
	CBV 100			PQ (5.2); $a_0 = 24.64$
Y, NH4Y	LZY-64, -84[d]	NH4	10	UOP (5.1, 5.9); $a_0 = 24.70, 24.57$
	CBV 300			PQ (5.2); $a_0 = 24.68$
Y, HY	LZY-74	H	10	UOP (5.2); $a_0 = 24.52$
	HZS-320HOA[d]			TOSOH (5.5); $a_0 = 24.50$
	HZS-330HSA[d]			TOSOH (6); $a_0 = 24.50$
	CBV 400, 500			PQ (5.1, 5.2); $a_0 = 24.50, 24.53$
Y, USY	LZ-10, -20	H, Al	10	UOP (5.5, 5.6); $a_0 = 24.30, 24.35$
	HSZ-330HUA[d]			TOSOH (5.6); $a_0 = 24.40$
	CBV 600			PQ (5.2); $a_0 = 24.33$
Y, dealuminate	LZ-210	H	10	UOP (6.5-18); a_0 varies
	HSZ-360,390HUA[d]			TOSOH(14,600); $a_0 = 24.30, 24.27$
	CBV 712-780			PQ (11.5-80); $a_0 = 24.33 - 24.24$
L	LZ-KL	K	8	UOP (6.3)
	HSZ-500KOA			TOSOH (6.2)
Mordenite, small-pore	AW-300	Na, mixed	4	UOP
Mordenite, large-pore	HSZ-610-640NAA	Na	7	TOSOH (12,15,20)
	CBV 10A			PQ (13)
	CBV 20, 30A	NH4		PQ (20,35)
	LZM-5 -8	H		UOP (10.7, 18)
	HSZ620, 640HOA			TOSOH (15, 16)

Table 2.7 (Continued).

Zeolite type	Designation	Cation	Effective pore diameter, Å	Unit cell parameter,[c] Å
Chabazite	AW-500	mixed	5	UOP
Ferrierite	HSZ-720KOA	K, Na	4	TOSOH (16.8)
ZSM-5	MFI, S-115	H	6	UOP (30–45, 180–400)
	HSZ-690HUA			TOSOH (>200)
	CBV 3020, 5020,			PQ (30, 50, 80, 150)
	8020, 1502			
Beta	CP 806B-25	Na, T[f]	7	PQ (25)
	CP 806BL-25	NH₄, T[f]		PQ (25)
	CP 811BL-25	H		PQ (25)
Zeolite F	Ionsiv F80	K, Na	4	UOP (2)
Zeolite W	Ionsiv W85	K, Na	4	UOP (3.6)

[a]Because of commercial usage, Angstrom units are shown here. To convert Å to nm, divide by 10.
[b]All zeolite types are available as powders unless otherwise indicated. Chabazite and Mordenite, small-pore are available as extrudates only.
[c]For (SiO_2/Al_2O_3) by manufacturer indicated.
[d]Also available as extrudate.
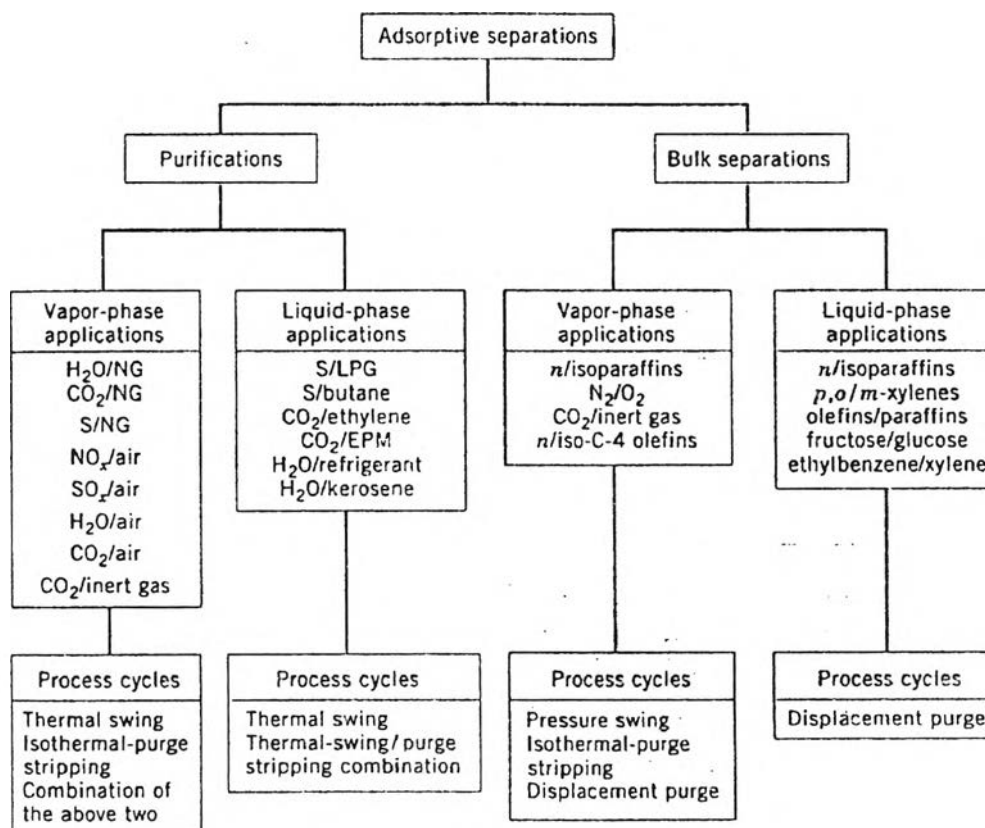[e]Also available as bead.
[f]T = template.

Figure 2.5 Classification of adsorptive separations where NG = natural gas and S = sulfur. EPM = ethylene-propylene rubber [1].

Table 2.8 UOP Sorbex processes for liquid-phase separations [3].

Process	Separation	Zeolite	Desorbent
Parex	p-Xylene from its isomers	KBaY SrBaX KBaX	Toluene p-Diethyl benzene
Ebex	Ethylbenzene from its isomers	NaY or SrKX	Toluene
Molex	n-Paraffins from isoparaffins, naphthalenes and aromatics	5A	Light paraffins
Olex	linear long-chain paraffins from other paraffins	CaX? SrX?	
Sarex	Fructose from sucrose and other sugars (corn syrup feed)	CaY	Aqueous system
Sorbutene	But-1-ene from C_4 olefins and paraffins		

The boiling point of o-xylene (144.1 °C) is 5 °C higher than that of m-xylene as shown in Table 2.9. Therefore, where only o-xylene is required, it can be separated directly by fractional distillation from the mixed xylenes. The boiling point of ethylbenzene is only 2 °C lower than p-xylene, therefore, direct separation of ethylbenzene by distillation is also possible. The very small difference in volatility between p-xylene and m-xylene, direct production of high purity p-xylene by distillation is not practically feasible. The separation is achieved either by crystallization or by an adsorption process such as Parex, a series of Sorbex processes [1,2].

Crystallization

Low temperature fractional crystallization was the first method for separating p-xylene from mixed xylenes. It was the only commercial technique for many years. As shown in Table 2.9, p-xylene has a much higher freezing point than the other xylene isomers. Thus, upon cooling, a pure solid phase of p-xylene crystallizes first at about -4 °C. Eventually, upon further cooling, a temperature is reached where solid crystals of another isomer also form. This point, the p-xylene-m-xylene eutectic, is reached at about -68 °C. In commercial practice, p-xylene crystallization is carried out at a temperature just about the eutectic point. At all temperatures above the eutectic point, p-xylene is still soluble in the remaining C_8-aromatics liquid solution, called

mother liquor, limiting the efficiency of crystallization processes to a per pass p-xylene recovery of about 60-65%. The solid p-xylene crystals are separated from the mother liquor by filtration (qv) or centrifugation. Good solid-liquid separation is important for obtaining high purity p-xylene.

Table 2.9 Physical properties for C_8-aromatic compounds [1].

Property	PX	MX	OX	EB
molecular weight	106.167	106.167	106.167	106.167
density at 25°C, g/cm^3	0.8610	0.8642	0.8802	0.8671
boiling point, °C	138.37	139.12	144.41	136.19
freezing point, °C	13.263	−47.872	−25.182	−94.975
refractive index at 25°C	1.4958	1.4971	1.5054	1.4959
surface tension , mN/m(=dyn/cm)	28.27	31.23	32.5	31.50
dielectric constant at 25°C	2.27	2.367	2.568	2.412
dipole moment of liquid, C·m	0	0.30	0.51	0.36
critical properties				
critical density, mmol/cm^3	2.64	2.66	2.71	2.67
critical volume, cm^3/mol	379.0	376.0	369.0	374.0
critical pressure, MPa	3.511	3.535	3.730	3.701
critical temperature, °C	343.05	343.90	357.15	343.05
thermodynamic properties at 25°C				
C_s, J/(mol·K)	181.66	183.44	188.07	185.96
S_s, J/(mol·K)	247.36	253.25	246.41	255.19
$H_o - H$, J/mol	44.641	40.616	42.382	40.219
$-(G_s - H_o)/T$, J/(mol·K)	97.633	117.03	104.46	120.29
heats of transition at 25°C, J/(mol·K)				
vaporization	42.036	42.036	43.413	42.226
formation	−24.43	−25.418	−24.439	−12.456
vapor pressure, Antoine equation				
A	6.1155	6.1349	6.1239	6.0821
B	1453.430	1462.266	1474.679	1424.255
C	215.307	215.105	213.686	213.206

PX : p-xylene

MX : m-xylene

OX : o-xylene

EB : ethylbenzene

As of the mid-1990s, about 40% of the p-xylene produced worldwide uses crystallization technology. The more common of crystallization processes are those developed by Chevron, Krupp, Amoco, Arco, and Phillips [1,2]. Figure 2.6 shows Chevron p-xylene crystallization process of two crystallizers in series operated at different pressure. The Amoco p-xylene crystallization process is a two-stage process that operates with indirect cooling, Figure 2.7.
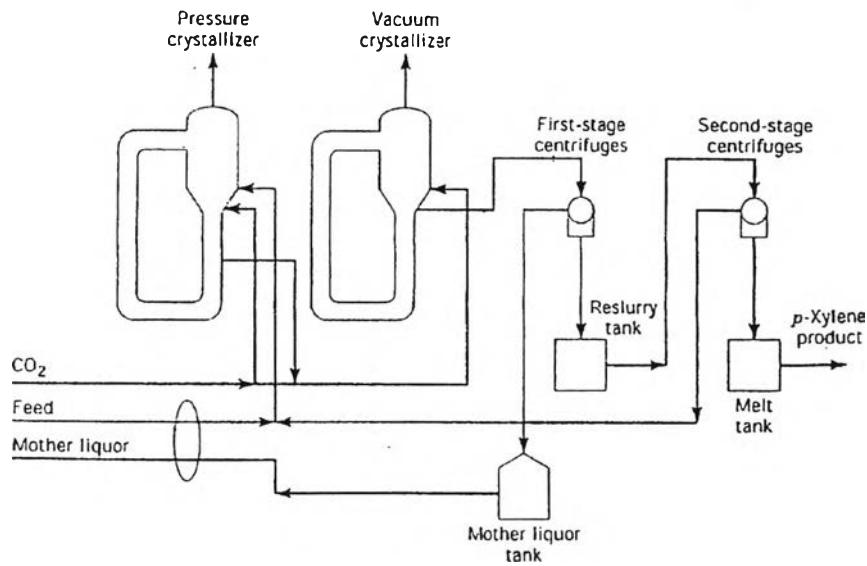
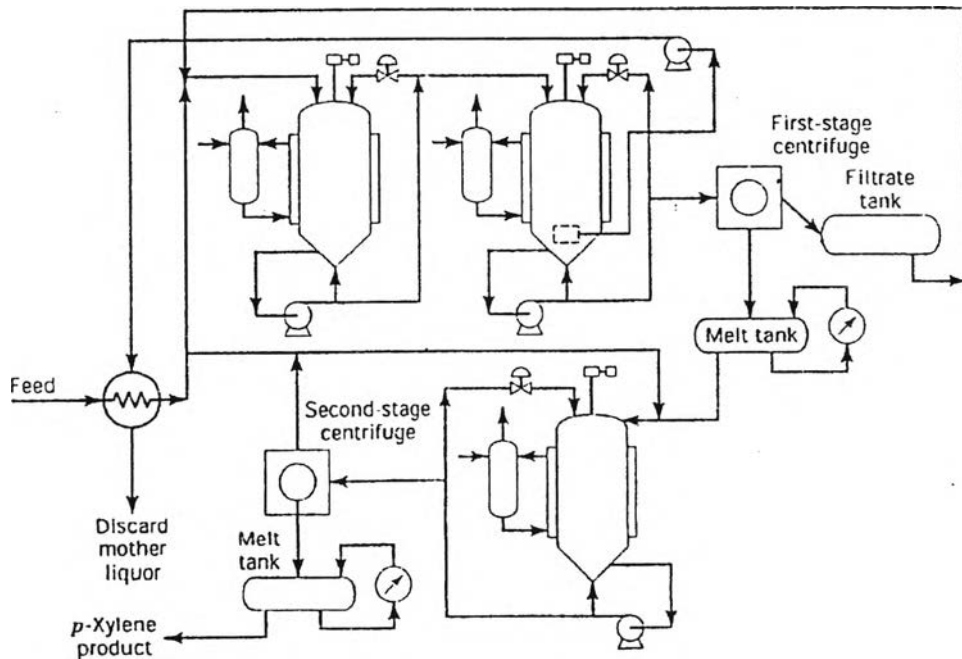**Figure 2.6** Chevron p-xylene crystallization process [1].

Figure 2.7 Amoco p-xylene crystallization process [1].

Adsorption processes

Adsorption is a newer method for separating and producing high purity p-xylene. In this process, adsorbents such as molecular sieves are used to produce high purity p-xylene by preferentially removing p-xylene from mixed xylenes stream. Typical p-xylene recovery per pass is over 95%, compared to only 60-65 % for

crystallization. Thus recycle rates to the separation and isomerization units are much smaller when adsorption is used.

There were three commercial p-xylene adsorption processes: UOP Parex, IFP Eluxyl, and Toray Aromax as of 1996. In all of these processes, the feed and desorbent inlets and the product outlet ports are moved around the bed simulating a moving bed.

Figure 2.8 shows the fixed-bed continuous adsorption process of UOP Parex process. The feed, desorbent, and product ports are continuously changed using a patented rotary valve. The operating condition is 250-400 °C and moderate pressures [1]. The adsorbent and desorbent are shown in Table 2.8.
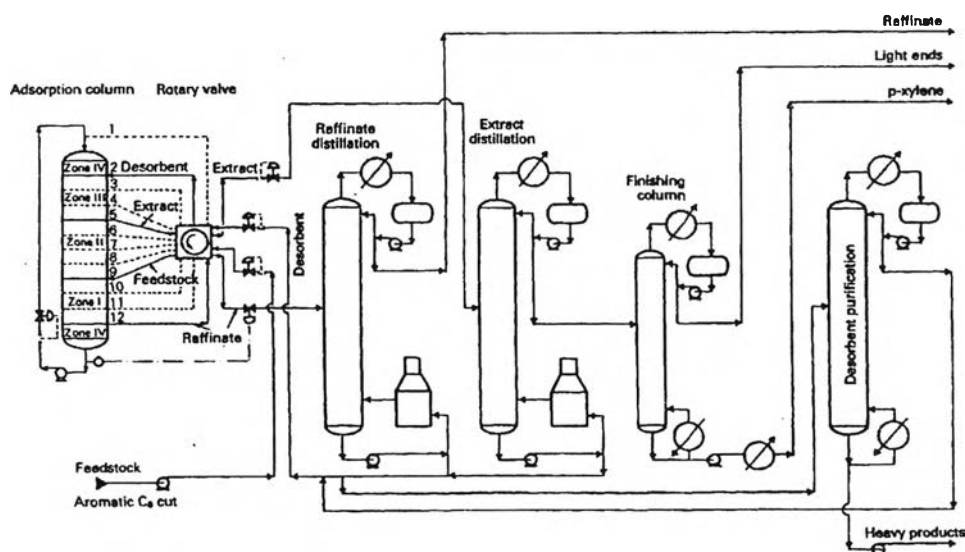
Figure 2.8 Separation of p-xylene by adsorption, UOP Parex process [14].

2.3 Membrane separation

Since membranes have widely used in separation processes such as reverse osmosis, ultrafiltration, pervaporation, gas permeation and so on as shown in Table 2.10, it is of much interest to use membrane such as the silicalite membrane which has hydrophobic/organophilic characteristic to separate mixed xylenes. Basically, a feed consisting of a mixture of two or more components is partially separated by means of a semipermeable barrier (the membrane) through which one or more species

move faster than another or other species. The most general membrane process is shown in Figure 2.9 where the feed mixture is separated into a retentate and a permeate. The feed, retentate, and permeate are usually liquid or gas, they may also be solid. The membrane is most often a thin, nonporous polymeric film, but may also be porous polymer, ceramic, or metal materials, or even a liquid or gas. The optional sweep, shown in Figure 2.9, is a liquid or gas, used to help remove the permeate.

Table 2.10 Industrial applications of membrane separation processes [15].

1. Reverse osmosis:
Desalinization of brackish water
Treatment of wastewater to remove a wide variety of impurities
Treatment of surface and ground water
Concentration of foodstuffs
Removal of alcohol from beer and wine
2. Dialysis:
Separation of nickel sulfate from sulfuric acid
Hemodialysis (removal of waste metabolites, excess body water, and restoration of electrolyte balance in blood)
3. Electrodialysis:
Production of table salt from seawater
Concentration of brines from reverse osmosis
Treatment of wastewaters from electroplating
Demineralization of cheese whey
Production of ultrapure water for the semiconductor industry
4. Microfiltration:
Sterilization of drugs
Clarification and biological stabilization of beverages
Purification of antibiotics
Separation of mammalian cells from a liquid
5. Ultrafiltration:
Preconcentration of milk before making cheese
Clarification of fruit juice
Recovery of vaccines and antibiotics from fermentation broth
Color removal from Kraft black liquor in paper-making
6. Prevaporation:
Dehydration of ethanol–water azeotrope
Removal of water from organic solvents
Removal of organics from water
7. Gas permeation:
Separation of CO_2 or H_2 from methane and other hydrocarbons
Adjustment of the H_2/CO ratio in synthesis gas
Separation of air into nitrogen- and oxygen-enriched streams
Recovery of helium
Reocvery of methane from biogas
8. Liquid membranes:
Recovery of zinc from wastewater in the viscose fiber industry
Recovery of nickel from electroplating solutions

In membrane separations: (1) the two products are usually miscible, (2) the separating agent is a semipermeable barrier, and (3) a sharp separation is often difficult to achieve. Thus, membrane separations differ in two or three of these

respects from the more common separation operations of absorption, stripping, distillation, and liquid-liquid extraction.
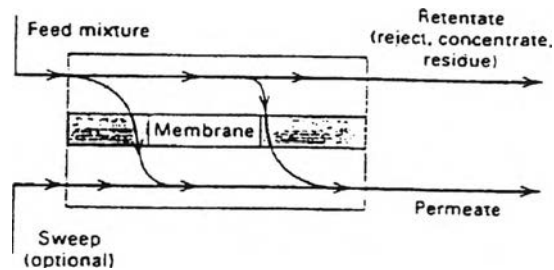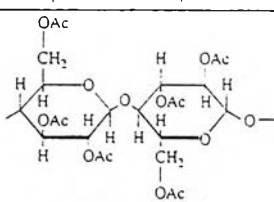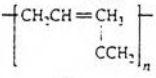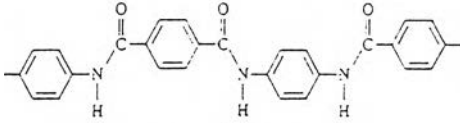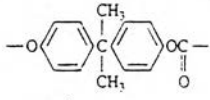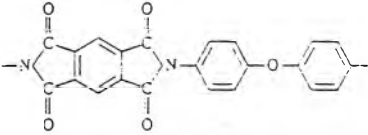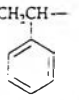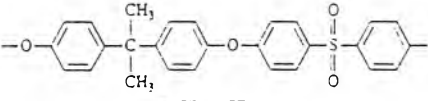

Figure 2.9 General membrane process [15].

The replacement of the more common separation operations with membrane separation has the potential to save large amounts of energy. This replacement requires the production of high mass-transfer flux, defect-free, long-life membranes on a large scale and the fabrication of the membrane into compact, economical modules of high surface area per unit volume. The key to an efficient and economical membrane separation process is the membrane and the manner in which it is packaged and modularized. Desirable properties of a membrane are (1) good permeability, (2) high selectivity, (3) chemical and mechanical compatibility with the processing environment, (4) stability, freedom from fouling, and reasonably useful life, (5) amenability to fabrication and packaging, and (6) ability to stand with the large pressure difference across the membrane thickness [15].

2.3.1 Membrane materials

Almost all industrial membranes processes are made from natural or synthetic polymers. Natural polymers include wool, rubber, and cellulose. Synthetic polymers are produced by polymerization of a monomer by condensation or addition, or by the copolymerization of two different monomers. Table 2.11 shows the common polymers used in membranes.

Table 2.11 Common polymers used in membranes [15].

Polymer	Type	Representative Repeat Unit	Glass Transition Temp., °C	Melting Temp. °C
Cellulose triacetate	Crystalline	(structure)		300
Polyisoprene (natural rubber)	Rubbery	$-[CH_2CH=CH_2\;CCH_3]_n-$	–70	
Aromatic polyamide	Crystalline	(structure)		275
Polycarbonate	Glassy	(structure)	150	
Polyimide	Glassy	(structure)	310–365	
Polystyrene	Glassy	$-CH_2CH-$	74–110	
Polysulfone	Glassy	(structure)	190	
Polytetrafluoroethylene (Teflon)	Crystalline	$-CF_2-CF_2-$		327

Polymer membranes can be dense or microporous. For dense amorphous membranes, no pores of microscopic dimensions are present, and diffusing species must dissolve into the polymer and then diffuse through the polymer between the segments of the macromolecular chains. Diffusion can be difficult, but highly selective for glassy polymers. If the polymer is partly crystalline, diffusion will occur almost exclusively through the amorphous regions, with the crystallite regions decreasing the diffusion area and increasing the diffusion path.

A microporous membrane contains interconnected pores that are small (on the order of 0.005-20 µm), but large in comparison to the size of small molecules. The pores are formed by a variety of proprietary techniques. Such techniques are
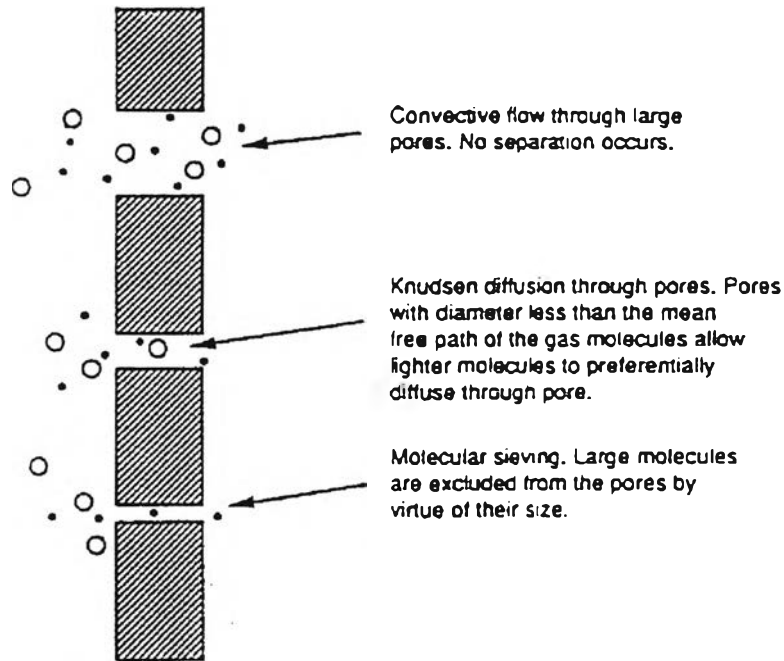
especially valuable for producing symmetric, microporous, crystalline membranes. Permeability for microporous membranes is high, but selectivity is low for small molecules. However, when molecules both smaller and larger than the pore size are in the feed to the membrane, the molecules may be separated almost perfectly by size.

The application of polymer membranes is generally limited to temperatures below about 200 °C and to the separation of mixtures that are chemically inert. When operation at high temperatures and/or with chemically active mixtures is necessary, membranes made of inorganic materials can be used. These include mainly microporous ceramics, metals, and carbon; and dense metals, such as palladium, that allow the selective diffusion of very small molecules such as hydrogen and helium [15].

2.3.2 Transport in membrane

The membranes can be macroporous, microporous, or dense (nonporous). Only microporous or dense membranes are permselective. However, macroporous membranes are widely used to support thin microporous and dense membranes when significant pressure differences across the membrane are necessary to achieve a reasonable throughout. Figure 2.10 show the mechanisms of transport in membranes. If the membrane contains pores large enough to allow convective flow, separation will not occur. If the size of the pores is smaller than the mean free path of the gas molecules, then convective flow is replaced by Knudsen diffusion. If the pores are small enough, large molecules are unable to pass through them and are excluded by the membrane. This molecular sieving is potentially useful in separating molecules of different sizes. The membrane currently used in most commercial applications are solution-diffusion membranes, Figure 2.10 B. These membranes are named because transport occurs when gas molecules dissolve into the membrane and then diffuse across it. while solution-diffusion membranes can be made of a liquid layer supported on a porous support [16].

A. POROUS MEMBRANES

Convective flow through large
pores. No separation occurs.

Knudsen diffusion through pores. Pores
with diameter less than the mean
free path of the gas molecules allow
lighter molecules to preferentially
diffuse through pore.

Molecular sieving. Large molecules
are excluded from the pores by
virtue of their size.

B. SOLUTION-DIFFUSION MEMBRANES

Gas dissolves into the membrane
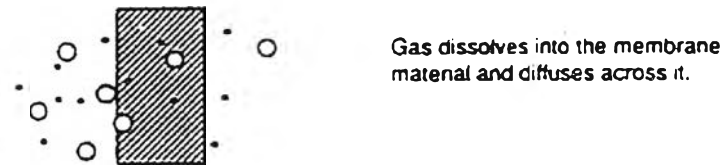material and diffuses across it.

Figure 2.10 Mechanisms of transport in membranes [16].

2.3.3 Gas permeation

In general, the separation of mixed xylenes uses the same principles of gas permeation. In gas permeation, shown in Figure 2.11, the feed gas, at high pressure P_1, contains some low molecular weight species (MW < 50) to be separated from small amounts of higher molecular weight species. Usually a sweep gas is not used, but the other side of the membrane is maintained at a much lower pressure, P_2, often near ambient pressure. The membrane, often dense but sometimes microporous, is permselective for certain of the low molecular weight species in the feed gas, shown in Figure 2.11 as the A species. If the membrane is dense, these species are absorbed at the surface and then transported through the membrane by one or more mechanisms. Thus, permselectivity depends on both membrane absorption and the

membrane transport rate. The products are a permeate that is enriched in the A species and a retentate that is enriched in B. A near-perfect separation is generally not achievable. If the membrane is microporous, as for example in high temperature applications, pore size is extremely important because it is usually necessary to block the passage of species B.
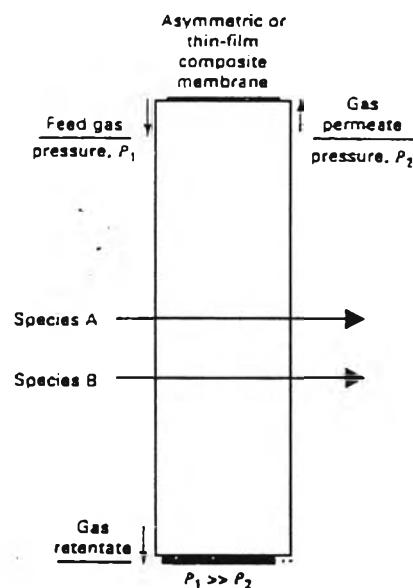

Figure 2.11 Gas permeation [15].

Gas permeation must compete with distillation at cryogenic conditions, absorption, and pressure-swing adsorption. Some of the advantages of gas permeation are low capital investment, ease of installation, ease of operation, absence of rotating parts, high process flexibility, low weight and space requirements, and low environmental impact. In addition, if the feed gas is already at so high a pressure that a gas compressor is not needed, then no utilities are required. Gas permeation separators are claimed to be relatively insensitive to changes in feed flow rate, feed composition, and loss of membrane surface area [15].

2.4 Silicalite

Silicalite is one type of zeolites which is a molecular sieve material. It has the same pore structure as ZSM-5 but it contains only silica in the structure. Figure 2.12

shows the channel systems of silicalite. It has two pore systems, one consisting of zigzag channels of near-circular cross section (5.4x5.6 Å) and another of straight channels of elliptical shape (5.1x5.7 Å) [17]. It has a specific gravity at 25 °C of 1.99 ± 0.05 g/cc as measured by water displacement and has specific gravity 1.70 ± 0.05 g/cc after calcined at 600 °C in air for 1 hour. Table 2.12 lists the data representing the x-ray powder diffraction pattern of a typical silicalite composition containing 51.9 moles of SiO_2 per mole of $(TPA)_2O$ which calcined in air at 600 °C for 1 hour [18].
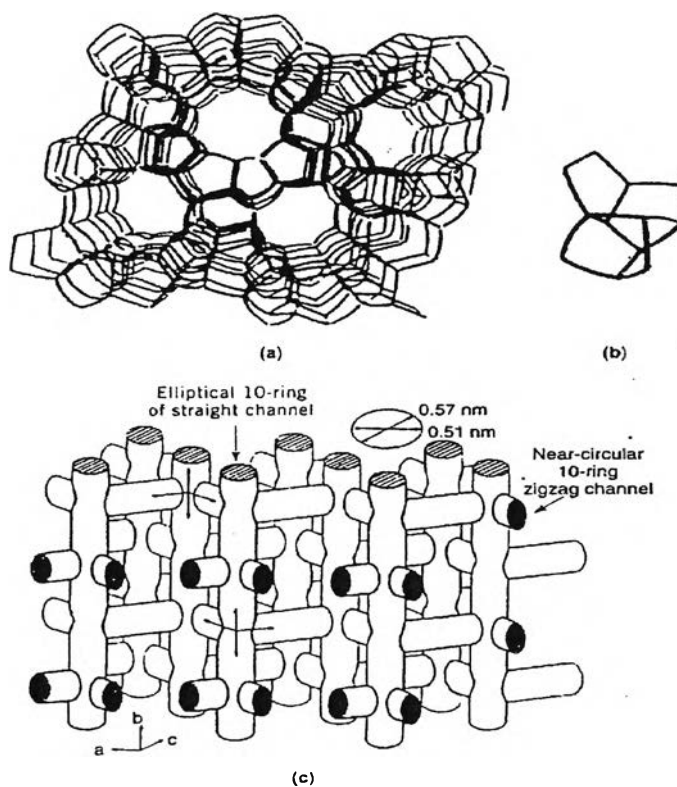
Figure 2.12 (a) Framework structure showing the topology of the molecular sieve ZSM-5 (silicalite) viewed in the direction of the main channel. (b) The 12-tetrahedra secondary building unit. (c) Idealized channel system in ZSM-5 [17].

Silicalite has a very low selectivity for the adsorption of water and a very high preference for the adsorption of organic molecules smaller than its limiting pore size. This hydrophobic/organophilic characteristic permits its use in selectively adsorbing organic materials from water either in liquid or vapor phase such as the research of concentration of alcohols by adsorption on silicalite [6] and potentials of silicalite membranes for the separation of alcohol/water mixtures [7]. Silicalite is capable of making size-selective separations of molecular species such as the separation of

hydrocarbon isomer vapors with silicalite membranes [8]. Silicalite is stable in air to over 1,100 °C and only slowly converts to an amorphous glass at 1,300 °C. It is stable to most mineral acids but reacts with HF similarly to quartz [17].

Table 2.12 XRD pattern of silicalite, calcined in air at 600 °C for 1 hour [18].

d-A	Relative Intensity	d-A	Relative Intensity
11.1	100	4.35	5
10.02	64	4.25	7
9.73	16	4.08	3
8.99	1	4.00	3
8.04	0.5	3.85	59
7.42	1	3.82	32
7.06	0.5	3.74	24
6.68	5	3.71	27
6.35	9	3.64	12
5.98	14	3.59	0.5
5.70	7	3.48	3
5.57	8	3.44	5
5.36	2	3.34	11
5.11	2	3.30	7
5.01	4	3.25	3
4.98	5	3.17	0.5
4.86	0.5	3.13	0.5
4.60	3	3.05	5
4.44	0.5	2.98	10

Baertsch et.al. investigated the permeation of aromatic hydrocarbon vapors through silicalite membranes [19]. The silicalite layers were synthesized on the inside of commercially available porous γ-alumina tubes. The average thickness of the silicalite layer was 2-10 μm. The membranes were characterized by gas permeation. It was found that vapor permeances of pure aromatics through silicalite membranes follow the relative order m-xylene > p-xylene > benzene ≈ toluene > ethylbenzene ≈ o-xylene near 380 K. This trend does not follow the size order of the kinetic diameters, and therefore the kinetic diameter is not the determining factor for the permeation. In addition, binary mixtures of p-xylene/o-xylene, p-xylene/ethylbenzene, p-xylene/toluene, and m-xylene/ethylbenzene and one ternary mixture of benzene, toluene, and p-xylene were used as feeds. In binary and ternary mixtures, the faster permeating compounds were slowed to rates similar to the slower permeating molecules, and thus no separation was obtained for any mixture in the temperature ranges of 380-480 K.

Funke et.al. investigated the separations of cyclic, branched, and linear hydrocarbon mixtures through silicalite membranes [20]. The silicalite layers were synthesized on the inside of commercially available porous γ-alumina tubes. The maximum thickness of the continuous layer was 2-10 μm. The membranes were characterized by gas permeation. It was found that:

1. The permeances of pure n-alkanes (C_5-C_9) monotonically decreased with increasing chain length. The bulkier branched and cyclic molecules were expected to permeate more slowly than the linear molecules in the silicalite pores. Almost all permeances increased with increasing temperature.

2. Mixtures of branched or cyclic molecules with small linear alkanes were readily separated with high selectivities, even though the ratios of pure component permeances were small. The separation behavior was not due to molecular sieving but instead appeared to be due to preferential adsorption of one species, which prevented the other organics from adsorbing and transporting through the membrane.