



UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND SORPTION PROPERTIES OF ZEOLITE ZSM-5

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By

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Zeolite ZSM-5 was synthesised by using SDS or the mixture of TPA/SDS as a templating agent. There is no significant difference in the X-Ray Diffraction (XRD) pattern observed among zeolites synthesised using different templating agents. This indicated that zeolites of similar crystallinity were formed. However, slightly different surface area, porosity and morphology of the zeolites were observed, when different ratio of TPA/SDS were used as a templating agents. Zeolites A, X and ZSM-5 were found to be an effective ion exchanger for lanthanum and yttrium ions from aqueous solutions. High metal ion uptake was achieved at initial pH solution of 4.0-4.5 with different conditions to avoid chemical precipitation. The microwave-assisted method showed that it could accelerate the metal sorption process by about 500 times compared to the conventional method. The zeolites loaded with lanthanum and yttrium ions significantly improved the sorption capacity of zeolite towards arsenic ions. Experimental conditions such as

pH, initial concentrations, adsorbent dosage and temperature have been optimised to utilise zeolite as an adsorbent for the removal of arsenate ion from aqueous solution. All data fitted the Langmuir and Freundlich isotherms. The zeolites were found to be an ineffective color removal agent for natural peat water and humic acid.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains.

SINTESIS DAN CIRI-CIRI ERAPAN ZEOLIT ZSM-5

Oleh

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Zeolit ZSM-5 telah disintesis dengan menggunakan SDS ataupun campuran TPA/SDS sebagai agen acuan. Tiada perbezaan yang ketara dalam corak belauan sinar x-raynya (XRD) diantara zeolit-zeolit yang disintesis menggunakan agen-agen acuan berbeza. Ini membuktikan bahawa zeolit ZSM-5 dengan kristal yang serupa telah terbentuk. Perbezaan dari segi keluasan, keliangan dan morfologi telah diperhatikan apabila nisbah yang berbeza bagi TPA/SDS digunakan. Zeolit-zeolit A, X dan ZSM-5 didapati amat sesuai digunakan sebagai penukar ion bagi ion-ion lantanum dan itrium dalam larutan akuas. Penukaran ion yang tinggi dapat diperolehi pada pH awal 4.0-4.5 dengan pembolehubah-pembolehubah yang berlainan untuk menghalang pemendakan secara kimia. Kaedah berbantuan mikrogelombang boleh digunakan untuk memacu proses erapan sehingga 500 kali lebih pantas berbanding dengan kaedah konvensional. Zeolit-zeolit yang dipadukan dengan ion logam lantanum dan itrium didapati dapat meningkatkan kapasiti erapan terhadap ion

arsenik. Beberapa pembolehubah eksperimen seperti pH, kepekatan bahan pemula, perubahan berat penyerap dan suhu telah digunakan untuk mengkaji zeolit sebagai penyingkir ion arsenat dalam larutan akuas. Semua data-data telah dipadankan dengan isoterma-isoterma Langmuir dan Freundlich. Zeolit-zeolit didapati tidak sesuai sebagai agen penyingkir warna untuk air tanah semulajadi dan asid humik.

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TABLE OF CONTENTS

	page
ABSTRACT	2
ABSTRAK	4
ACKNOWLEDGEMENTS	6
APPROVAL SHEETS	7
DECLARATION	9
TABLE OF CONTENTS	10
LIST OF TABLES	13
LIST OF FIGURES	14
LIST OF PLATES	17
LIST OF ABBREVIATIONS	18

CHAPTER

1	INTRODUCTION	20
	1.1 Zeolites	20
	1.1.1 Type of Zeolite	21
	1.1.2 Structure of Synthetic Zeolite	22
	1.1.3 Si/Al Ratios	24
	1.1.4 Exchangeable Cations	26
	1.1.5 Cavities and Channels	26
	1.1.6 Preparation of Zeolites	27
	1.2 Properties of Zeolites	30
	1.2.1 Adsorption and Separation	30
	1.2.2 Sorption of Metal Ions on Zeolites	31
	1.2.3 Ion Exchange	32
	1.2.4 Microwave-assisted Method	35
	1.3 Removal of Arsenic Ion	37
	1.4 Humic Substances	40
	1.5 Adsorption Isotherms	41
	1.5.1 Langmuir Isotherm	41
	1.5.2 Freundlich Isotherm	42
	1.5.3 Brunauer Emmet Teller (BET) Isotherm	43
	1.5.4 Type of Adsorption Isotherms	43
	OBJECTIVES OF STUDY	45
2	MATERIALS AND METHOD	46
	2.1 Materials for Zeolite ZSM-5 Synthesis	46
	2.2 Materials Used As Adsorbent	46
	2.3 Materials Used in the Sorption Studies	46
	2.4 Synthesis of Zeolite ZSM-5	47
	2.5 Sorption of Metal Ions on Zeolites	47

2.6	Sorption of Arsenic Ion on Zeolites and Metal-loaded Zeolites	48
2.7	Color Removal of Natural Peat Water by Zeolite A and Zeolite X	49
2.7.1	PECOL Color Software	49
2.8	Characterization of Zeolite ZSM-5	51
2.8.1	Adsorption, Surface Area and Porosity	51
2.8.2	Fourier Transform Infrared (FTIR) Spectroscopy	51
2.8.3	X-Ray Diffraction (XRD)	52
2.8.4	Scanning Electron Microscopy and Energy Dispersive X-ray Analyses	52
3	RESULTS AND DISCUSSION	53
3.1	Synthesis of Zeolite ZSM-5	53
3.1.1	XRD Patterns of Zeolite ZSM-5	53
3.1.2	Morphology of Zeolite ZSM-5	55
3.1.3	Surface Analysis	60
3.1.4	FTIR Spectra of Zeolite ZSM-5	60
3.2	Sorption Properties	63
3.2.1	General Equation for the Sorption Study	63
3.3	Sorption of Lanthanum and Yttrium Ions on Zeolites	63
3.3.1	Effect of pH on the Metal Ions Uptake	63
3.3.2	Speciation of Lanthanum and Yttrium at Various pH	65
3.3.3	Sorption Kinetics	68
3.3.4	Effect of Initial Metal Ion Concentrations	68
3.3.5	Effect of pH on Metal Ions	72
3.3.6	Effect of the Adsorbent Dosage on the Sorption of Metal Ions	75
3.3.7	Sorption of Metal Ions at Various Temperature	78
3.3.8	Adsorption Isotherm for the Adsorption of Metal Ion on Zeolites	78
3.4	Effect of pH on the Sorption Process	82
3.4.1	Adsorption-desorption Isotherms	82
3.4.2	FTIR Spectra of Metal-loaded Zeolites	85
3.4.3	XRD Patterns of Metal-loaded Zeolites	85
3.5	Removal of Arsenate Ion by Zeolites	90
3.5.1	Effect of pH on the Arsenate Uptake by Zeolites	90
3.5.2	Sorption of Arsenate by Metal-loaded Zeolite	90
3.5.3	Effect of Different Initial Arsenate Ion Concentrations	92
3.5.4	Effect of Different Initial Arsenate Ion Concentrations	92
3.5.5	Effect of the Adsorbent Dosage on the Removal of Arsenate	95

3.5.6	Sorption at Various Temperature	95
3.5.7	Adsorption Isotherm for the Removal of Arsenate Ion	98
3.6	Color Removal of Natural Peat Water	101
3.6.1	Determination of Concentration Humic Acid in Natural Peat Water	101
3.6.2	Effect of Contact Time	101
3.6.3	Effect of Adsorbent Dosage	103
4	CONCLUSION	108
	BIBLIOGRAPHY	111
	APPENDIX	116
	APPENDIX 1	117
	BIODATA OF AUTHOR	118

LIST OF TABLES

Table		Page
1	Zeolite Compositions.	22
2	The Effect of Templating Agent to the Surface Area, Porosity, Morphology and Si/Al Ratio of Zeolite ZSM-5.	59
3	Constants from the Langmuir and Freundlich Equations.	78
4	Type of Isotherms of Metal-loaded Zeolites at Different Initial pH.	82
5	Constants from the Langmuir and Freundlich Equations.	98

LIST OF FIGURES

Figure		Page
1	Primary building unit of zeolite (a), sodalite unit (b), structure of zeolite A (c), zeolite X (d) and zeolite ZSM-5 (e) [8].	25
2	The five type of adsorption isotherm, I to V in the classification of BET and type VI, the stepped isotherm [59].	44
3	Opponent type color scales [56].	50
4	XRD patterns of ZSM-5 synthesised with different TPA/SDS ratios, 1:0(a), 1:1(b), 1:3(c), 1:9(d) and 0:1(e).	54
5	Adsorption-desorption isotherms of N_2 (g) at 77K on zeolite ZSM-5 synthesised with different ratios of TPA/SDS, 1:0(a), 1:1(b), 1:3(c), 1:9(d) and 0:1(e).	61
6	IR spectra of the zeolite ZSM-5 synthesised with different ratios of TPA/SDS, 1:0(a), 1:1(b), 1:3(c), 1:9(d) and 0:1(e).	63
7	Capacity of La^{3+} and Y^{3+} on adsorbent at different equilibrium pH; zeolite A and X (a) and ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL of 5 mM metal ion solutions.	64
8	The dependency of final pH to the initial pH solution due to the introduction of the adsorbent zeolite A and X (a), and ZSM-5(T) and ZSM-5(S) (b).	66
9	The effect of pH on lanthanum and yttrium ions in solution. Conditions: initial lanthanum and yttrium ion concentration, 5 mM.	67
10	Sorption of La^{3+} and Y^{3+} on zeolites A and X(a) and ZSM-5(T) and ZSM-5(S) (b) by conventional method. Conditions: 0.1 g adsorbent in 25 mL of 5 mM metal ion solutions.	69
10(c)	Sorption of La^{3+} and Y^{3+} on zeolites A and X by microwave-assisted method. Conditions: 0.1 g adsorbent in 25 mL of 5 mM metal ion solutions.	70
11	The effect of lanthanum and yttrium initial concentration (pH 4.0) on sorption capacity for zeolite A and X (a), and zeolite ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL of 1-15 mM metal ion solutions.	71
12	Effect of initial metal ions concentration on final pH of solution.	73

13	Concentration of sodium ion in the solution at equilibrium after the sorption of La^{3+} and Y^{3+} on zeolite at constant pH; zeolite A and X(a), and zeolite ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL of 5 mM metal ion solutions.	76
14	The effect of the adsorbent dosage on the capacity of La^{3+} and Y^{3+} ions by zeolite A and X (a) and zeolite ZSM-5(T) and ZSM-5(S) (b). Conditions: 25 mL (pH 4.0) and initial metal ion concentration 6mM.	77
15	The effect of temperature on the sorption of lanthanum and yttrium on zeolite A and X (a), and zeolite ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL of 5 mM metal ion solutions. Equilibrium time 20 minutes.	79
16	Linearized Langmuir isotherm for sorption of lanthanum and yttrium on zeolites A and X (a), and zeolites ZSM-5(T) and ZSM-5(S) (b).	80
17	Linearized Freundlich isotherm for sorption of lanthanum and yttrium on zeolites A and X (a), and zeolites ZSM-5(T) and ZSM-5(S) (b).	81
18	Adsorption-desorption isotherms of N_2 (g) at 77K on the resulting La^{3+} and Y^{3+} on zeolite A, A-La (a) and A-Y (b) systems.	83
19	Adsorption-desorption isotherms of N_2 (g) at 77K on the resulting La^{3+} and Y^{3+} on zeolite X, X-La (c) and X-Y (d) systems.	84
20	IR spectra of La^{3+} and Y^{3+} -loaded on zeolites A, A-La (a) and A-Y (b).	86
21	IR spectra of La^{3+} and Y^{3+} -loaded on zeolites X, X-La (a) and X-Y (b)	87
22	XRD patterns of La^{3+} and Y^{3+} -loaded on zeolites A, A-La (a) and A-Y (b) systems.	88
23	XRD patterns of La^{3+} and Y^{3+} -loaded on zeolites X, X-La (a) and X-Y (b) systems.	89
24	The dependency of final pH of solution of arsenate ion to the sorption capacity on zeolites A and X (a) and zeolites ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL of 1 mM As (V) solution.	91

- 25 Effect of pH on the sorption of arsenate ion on (La³⁺ and Y³⁺)-loaded zeolites A and X (a) and (La³⁺ and Y³⁺)-loaded zeolites ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL of 3 mM sodium arsenate solution. 93
- 26 The effect of arsenate ion to initial concentration at pH 5.0 to the (La³⁺ and Y³⁺)-loaded zeolites A and X (a) and (La³⁺ and Y³⁺)-loaded zeolites ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL and C; prepared in the range of 1-5 mM As (V) solution. 94
- 27 The effect of dosage on the capacity of arsenate ion on (La³⁺ and Y³⁺)-loaded zeolites A and X (a) and (La³⁺ and Y³⁺)-loaded zeolites ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1g-0.5g adsorbent in 25 mL of 3 mM As (V) solution. 96
- 28 The effect of temperature on the sorption of arsenate ion on (La³⁺ and Y³⁺)-loaded zeolites A and X (a) and (La³⁺ and Y³⁺)-loaded zeolites ZSM-5(T) and ZSM-5(S) (b). Conditions: 0.1 g adsorbent in 25 mL of 3 mM As(V) solution. Equilibrium time 20 minutes. 97
- 29 Linearized Langmuir isotherm for the sorption of arsenate ion on (La³⁺ and Y³⁺)-loaded zeolites A and X (a) and (La³⁺ and Y³⁺)-loaded zeolites ZSM-5(T) and ZSM-5(S) (b). 99
- 30 Linearized Freundlich isotherm for the sorption of arsenate ion on (La³⁺ and Y³⁺)-loaded zeolites A and X (a) and (La³⁺ and Y³⁺)-loaded zeolites ZSM-5(T) and ZSM-5(S) (b). 100
- 31 The effect of contact time on color difference (ΔE_{ab}) of natural peat water (a) and humic acid (b) for zeolite A and X. 102
- 32 The effect of adsorbent dosage on color difference (ΔE_{ab}) of natural peat water (a) and humic acid (b) for zeolite A and X. 104
- 33 The effect of contact time on amount of magnesium (a) and calcium (b) ions sorbed on zeolite A and zeolite X. PW : peat water and HA : humic acid. 105
- 34 The effect of contact time on amount of iron (a) and sodium (b) ions sorbed on zeolite A and zeolite. PW : peat water and HA : humic acid. 106
- 35 The effect of contact time on amount of zinc (a) and manganum (b) ions sorbed on zeolite A and zeolite X. PW : peat water and HA : humic acid. 107

LIST OF PLATES

Plate		page
1	SEM micrograph of zeolite ZSM-5 by using TPA:SDS (1:0).	56
2	SEM micrograph of zeolite ZSM-5 by using TPA:SDS (1:1).	56
3	SEM micrograph of zeolite ZSM-5 by using TPA:SDS (1:3).	57
4	SEM micrograph of zeolite ZSM-5 by using TPA:SDS (1:9).	57
5	SEM micrograph of zeolite ZSM-5 by using TPA:SDS (0:1).	58

LIST OF ABBREVIATIONS

α	:	Limiting amount of metal ion that can be taken per mass of adsorbent
ΔE_{ab}	:	Color difference unit
ΔE_{ab-A}	:	Color difference value for zeolite A
ΔE_{ab-X}	:	Color difference value for zeolite X
A-La	:	Sorption of Lanthanum on zeolite A
ALa-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite A
A-Y	:	Sorption of Yttrium on zeolite A
AY-As	:	Sorption of Arsenate ion on Yttrium-loaded zeolite A
BET	:	Brunnauer Emmet Teller
C_e	:	Metal ion concentration at equilibrium (mM)
C_i	:	Initial metal ion concentration (mM)
EC	:	Euhedral Crystal
HA	:	Humic acid
K_F	:	Constant of Freundlich equation
K_L	:	Constant of Langmuir equation
n	:	Parameter of Freundlich equation
n_m	:	Monolayer capacity
P	:	Pressure
P°	:	Saturation pressure
PW	:	Peat water
pH_e	:	pH value at equilibrium
q_e	:	Capacity (mmol/g)

r	:	Correlation coefficient
S	:	Amount of zeolite (g)
SA	:	Spherulitic Agglomerates
t	:	Time
V	:	Volume of the solution (L).
X-La	:	Sorption of Lanthanum on zeolite X
XLa-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite X
X-Y	:	Sorption of Yttrium on zeolite X
XY-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite X
ZSM-5(S)La-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite ZSM-5 with SDS as a templating agent
ZSM-5(S)Y-As	:	Sorption of Arsenate ion on Yttrium-loaded zeolite ZSM-5 with SDS as a templating agent
ZSM-5(T)La-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite ZSM-5 with TPA as a templating agent
ZSM-5(T)Y-As	:	Sorption of Arsenate ion on Yttrium-loaded zeolite ZSM-5 with TPA as a templating agent
ZSM-5(S)-La	:	Sorption of Lanthanum on zeolite ZSM-5 with SDS as a templating agent
ZSM-5(S)-Y	:	Sorption of Yttrium on zeolite ZSM-5 with SDS as a templating agent
ZSM-5(T)-La	:	Sorption of Lanthanum on zeolite ZSM-5 with TPA as a templating agent
ZSM-5(T)-Y	:	Sorption of Yttrium on zeolite ZSM-5 with TPA as a templating agent

CHAPTER 1

INTRODUCTION

1.1 Zeolites

Zeolites are crystalline, hydrated aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations normally of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium, as well as water molecules in their structural frameworks. Structurally, they are complex, porous, crystalline inorganic polymers, enclosing interconnected cavities in which the metal ions and water molecules are contained. They are based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygen ions [1].

Zeolites may be represented by an empirical formula of $\text{M}_{2/n}\text{Al}_2\text{O}_3\text{xSiO}_2\cdot\text{yH}_2\text{O}$. In this oxide formula, x is generally equal to 2 or greater since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, n is the cation valence which neutralize the negative charge on the aluminosilicate framework and y represents the water contained in the voids of the zeolite [2].

The framework contains channels and interconnected voids that are occupied by the cation and water molecules. The cations are quite mobile and may usually be exchanged, to varying degrees, by other cations. Intracrystalline 'zeolitic' water in many zeolites is removed continuously and reversibly, generally by the application of heat, which leaves intact a crystalline host structure permeated by

micropores which may amount to 50% of the crystals by volume. In many other zeolites, mineral and synthetic, cation exchange or dehydration may produce structural changes in the framework.

A Swedish mineralogist Baron Axel Cronstedt first described zeolite as a mineral group in 1756. He named the mineral zeolite from the greek words *zeo* and *lithos* which means to boil and stone, respectively. Cronstedt observed that on heating with a blowtorch the zeolites hissed and bubbled as though they were boiling [2].

Zeolites are important inorganic materials, which have excellent catalytic as well as separation properties. Several properties of zeolite minerals have been studied, including adsorption and ion exchange. These were important applications of zeolites for removal of heavy metals by both processes. Among others, the advantages of ion exchange over the chemical precipitation method are high selectivity, can be recovered and produce less sludge. The availability of natural zeolites provides a low cost ion exchanger [3].

1.1.1 Type of Zeolite

Naturally, zeolite minerals are formed over much of the earth's surface, including the sea bottom. They were considered as typically occurring in nature in vugs and vesicles of basaltic lava in specific kinds of rocks subjected to moderate geologic temperature and pressure (the metamorphic zeolite facies) and in altered and reacted volcanic ash deposits [4]. They were widely used until 1948 when the

first pure synthetic of modernite was synthesised, while zeolites A, X and Y were synthesised by Union Carbide in 1956-64 and highly siliceous zeolite ZSM-5 (Zeolite Scony Mobil) was synthesised by Mobil Oil Corporation in 1972 [5]. Table 1 showed a few examples of zeolite composition [6].

Table 1: Zeolite Compositions

Zeolite	Typical formula
Natural	
Mordenite	$\text{Na}_8[\text{AlO}_2]_8(\text{SiO}_2)_{40} \cdot 24\text{H}_2\text{O}$
Faujasite	$(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)_{4.5}[\text{AlO}_2]_{59}(\text{SiO}_2)_{27} \cdot 27\text{H}_2\text{O}$
Clinoptilolite	$\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$
Synthetic	
Zeolite A	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$
Zeolite X	$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$
Zeolite ZSM-5	$(\text{Na}, \text{TPA})_3[(\text{AlO}_2)_3(\text{SiO}_2)_{93}] \cdot 16\text{H}_2\text{O}$

1.1.2 Structure of Syntbetic Zeolite

The fundamental building block of all zeolites is a tetrahedron of four oxygen anions surrounding a small silicon or aluminium ion. These tetrahedra are arranged so that each of the four oxygen anions is shared in turn with another silica or alumina tetrahedron to form a wide range of small secondary building units. The crystal lattice extends in three dimensions and the -2 oxidation state of each oxygen is accounted for. Each silicon ion has its +4 charge balanced by the four tetrahedral oxygen's and the silica tetrahedra and therefore electrically neutral.

Each alumina tetrahedron has a residual charge of -1 since the trivalent aluminium is bonded to four oxygen anions. It requires a + 1 charge from a cation in the structure to maintain neutrality. Figure 1(a) shows the primary building units of

zeolite. In these structural diagrams the corners of the polyhedra represent Si or Al atoms, and the connecting lines represent the shared oxygen atoms. The cations are usually sodium in zeolites as it is initially prepared, but they are readily replaced via ion exchange. This cation is not locked into the framework by a 'box' of four oxygen atoms as in the Si^{4+} or Al^{3+} . These charge compensating cations are relatively mobile and can in many cases easily exchanged for other cations [6]. Ion exchange represents the most direct and useful method for the alteration of zeolite properties.

Many zeolite structures are based on a secondary building unit that consists of 24 silica or alumina tetrahedra linked together. For example 4 and 6 rings linked together to form a basket like structure called a truncated octahedron. This is a sodalite unit (or β -cage) as shown in figure 1(b). Several of the most important zeolite structures are based on the sodalite unit (a truncated octahedron). Different combinations of the same secondary building unit may give numerous distinctive zeolites.

The structure of a synthetic zeolite, zeolite A is shown in figure 1(c). Oxygen bridges between the 4 rings linked each sodalite unit. A three dimensional network of linked cavities forming channels is formed. The free pore aperture of zeolite A is determined by an eight member oxygen ring and it has a free pore diameter of 4.2 Å [7].

The structure of faujasite [7], a naturally occurring mineral, is shown in figure 1(d). The sodalite units are linked by oxygen bridges between four of the

eight 6 rings in a tetrahedral array, forming hexagonal prisms. The truncated octahedra are stacked similar to those carbon atoms in diamond. This structure result in a supercage (sorption cavity) surrounded by ten sodalite units, which is sufficiently large for an inscribed sphere with a diameter of 12 Å.

The framework of ZSM-5 which were determined by Kokotailio *et al.* [8] contains a novel configuration of linked tetrahedra shown in figure 1(e) and consisting of eight five membered rings. Then, the ZSM-5 units join through edges to form chains. The chains can be connected to form sheets and the linking of the sheet lead to a three dimensional framework structure. The chains extend along the z-axis. The generic name 'pentasil' has been given to designate these solids, irrespective of minor differences in crystal structure. The ZSM-5 framework contains two intersecting channel systems, one sinusoidal running parallel to 001 and the other straight and parallel to 010.

1.1.3 Si/Al Ratios

The Si/Al ratio of a zeolite could showed the changes of its cation content; the fewer aluminium atoms there are, the fewer the exchangeable cations will be present. The highly siliceous zeolites such as zeolite ZSM-5 can have a Si/Al ratio that lies between 20 and ∞ . Zeolite A and X have Si/Al ratio of 1. Zeolites with high Si/Al ratios are stable in the presence of concentrated acids but not to those with lower Si/Al ratios (in ratio 1-1.5) [7].