PRODUCTION OF ZEOLITES FROM OIL PALM ASH

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ABSTRACT

In this research, the ability of oil palm ash to produces value added product such as zeolites is studied. Characterization of oil palm ash from one of the palm oil plantation in Malaysia has been carried out and used for the production of zeolites. The production of zeolites from oil palm ash appears to be one of the alternatives in the utilization of waste materials. The method used to produce zeolites is alkaline hydrothermal treatment .The characterization analysis of oil palm ash and zeolites are diffraction pattern, morphological structure, and chemical composition. The characterization equipment involved is X-Ray diffraction (XRD), scanning electron microscopy (SEM) and X-Ray fluorescence (XRF). The experiment is conducted at laboratory of FKKSA UMP while some characterization analysis is carried out at laboratory of environmental analysis at UTHM. From the mineralogical studies carried out, it was found that silica and alumina were the major component of oil palm ash and zeolites. The maximum condition for production of zeolites is at 1:3 NaOH/OPA ratio, hydrothermal temperature 80°C and hydrothermal time 6 hour. The present result is very much useful in opening up way to produce zeolites at low cost with useful application.

Keywords: oil palm ash, zeolites, hydrothermal, characterization and low cost

ABSTRAK

Di dalam kajian ini, keupayaan abu kelapa sawit untuk menghasilkan produk tambahan yang bernilai seperti zeolit telah dikaji. Pencirian abu kelapa sawit dari salah sebuah ladang kelapa sawit di Malaysia telah dilakukan dan digunakan untuk menghasilkan zeolit. Penghasilan zeolit dari abu kelapa sawit merupakan salah satu alternatif dalam pengunaan semula bahan-bahan buangan. Kaedah yang digunakan untuk menghasilkan zeolit ialah kaedah alkali hidrotermal. Analisis pencirian yang dijalankan terhadap abu tandan dan zeolit ialah ujian pola pembelauan, struktur morfologi dan komposisi kimia. Alat ujikaji yang terlibat dalam analisis pencirian ialah pembelauan sinar X (XRD), pengimbas mikroskop elektron (SEM) dan pendafluoran sinar X (XRF). Eksperimen telah dilakukan di makmal FKKSA UMP manakala sebahagian analisis pencirian dijalankan di makmal analisis persekitaran UTHM. Berdasarkan kajian mineralogi yang dilakukan, silika dan alumina merupakan major komponen di dalam abu kelapa sawit dan zeolit. Kondisi maksima untuk menghasilkan zeolit adalah pada 1:3 NaOH/abu kelapa sawit, suhu hidrotermal 80°C, dan masa hidrotermal 6 jam. Hasil yang diperolehi seterusnya sangat bermanfaat bagi membuka ruang untuk penghasilan zeolit pada kos yang rendah di samping pengunaan yang meluas.

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LIST OF ABBREVIATION

EFB	Empty fruit bunch
FFB	Fresh fruit bunch
R&D	Research & Development
OPA	Oil palm ash
SO_2	Sulfur dioxide
XRD	X-ray diffraction
LP	Large particles
MP	Medium particles
SP	Small particles
SiO_2	Silicon dioxide
K_2O	Kalium oxide
CaO	Calcium oxide
P_2O_5	Potassium oxide
MgO	Magnesium oxide
Al_2O_3	Aluminum oxide
C	Carbon
Fe_2O_3	Ferum oxide
CO_2	Carbon dioxide
Na_2O	Natrium oxide
TiO_2	Titanium oxide
MnO	Manganese oxide
$[SiO_4]^{4-}$	Silicate ion
$[AlO_4]^{5-}$	Aluminates ion
K	Kalium

Na	Natrium
Mg	Magnesium
Ca	Calcium
Sr	Strontium
Ba	Barium
H_2O	Water
Si	Silicon
Al	Aluminum
Fe^{3+}	Ferum ion
LTA	Zeolite A
LTL	Zeolite L
BEA	Zeolite Beta
GIS	Gismondine
MFI: ZSM-5	Zeolite Socony Mobile No.5
MOR	Mordenite
IUPAC	International Unit
NH_3	Ammonia
N_2	Nitrogen gas
O_2	Oxygen gas
NaOH	Natrium hydroxide
$NaNO_3$	Natrium nitrate
KNO_3	Kalium nitrate
CEC	Cation exchange
SEM	Scanning electron microscopy
XRF	X-ray fluorescence
UMP	Universiti Malaysia Pahang
UTHM	Universiti Tun Hussein Onn Malaysia
TPD	Temperature-programmed desorption

LIST OF SYMBOLS

μm	Micrometer
%	Percent
h	Hour
°C	Celcius
m^2/g	meter square per gram
g	gram
ml	mililiter
t	time

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Malaysia is one of the world leaders in the production and export of palm oil. The total exports of oil palm products, constituting of palm oil, palm kernel oil, palm kernel cake, oleo chemicals and finished products reached 20.13 million tons in 2006 from 18.62 million tons recorded in 2005 (Basri, 2006). However, these industries also generate various pollutants of the environment which is the production of palm oil creates large quantity of solid waste by-products. The waste material, oil palm ash, is an undesired collected material procured from the boilers after combustion of palm fibers and shells (Hameed et. al., 2008). The abundance of agro waste from oil palm industries in Malaysia has inspired researcher to utilize the potential usage of this waste as a main composition to produce zeolites.

Oil palm ash is a by-product obtained from a small power plant, which uses the palm fiber, shells and empty fruit bunches as a fuel and burnt at 800- 1000ºC. The main chemical composition of oil palm ash is silica which is have great similarities with the raw materials typically used in the manufacture of zeolites.

The motivation for using this source as the starting materials in production of zeolites is driven by factors, such as they are cheap and available in bulk quantities, are currently under-utilized, have high workability, and require less water (or solution) for activation. The production of zeolites using oil palm ash also as a resource constitutes one important solution of waste management.

Zeolites, thank to its properties resulting from their composition which is predominantly silica. Zeolites comprise a large group of microporous, crystalline solids with well-defined structures that contain mainly aluminium, silicon and oxygen in their regular framework as well as cations and water in the pores (Weitkamp and Puppe, 1999). The preparation of synthetic zeolites from chemical reagents is expensive. Therefore, in order to reduce costs, zeolites researchers are seeking cheaper aluminosilicate bearing raw materials, such as oil palm ash, to produce synthetic zeolites. This research is concerned with the production of zeolites from of oil palm ash by using alkali treatment method.

1.2 Problem Statement

The amount of oil palm ash generated from oil palm industries has been increasing throughout the world. Alternative economic disposal methods are necessary and one potential method is to convert the wastes into useful product. Empty oil-palm fruit bunches discharged from the mill is currently being disposed of by burning in an incinerator. After combustion, a substantial amount of ash is produced which creates problems of disposal. The dumped oil palm ash may be a significant resource for zeolites production. Beside that, demand for an easily accessible and inexpensive source of zeolites has raised interest in production of zeolites. The extraction of natural zeolite deposits is more expensive and cause considerable degradation of the environment. This research is introduced as a solution to waste management. It is also to motivate the production of zeolites by using low cost material such as oil palm ash.

1.3 Research Goal

1. To produce zeolites from oil palm ash using alkaline hydrothermal treatment method
2. To obtain the effect of NaOH/OPA ratio , hydrothermal time and hydrothermal temperature on the SiO_2/ Al_2O_3 ratio in zeolites
3. To analyze the characterization of zeolites resulting from oil palm ash

1.4 Research Advantage

1. Production of value added product from waste can be seen as a solution to waste management
2. Agro waste of oil palm is abundance and can be obtained without any cost incurred
3. Zeolites can be produced from low cost material and can fulfill industrial needed
4. The process is environmental friendly
5. Contribution to the society in preventing the community from any harm and danger for instance air pollution

1.5 Scope of Research

1. Production of zeolites from oil palm ash by using alkaline hydrothermal method.
2. Obtaining the effect of NaOH/OPA ratio , hydrothermal treatment time and temperature on the SiO_2/ Al_2O_3 ratio in zeolites
3. Analyzing the characterization of zeolites resulting from oil palm ash

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Oil Palm Ash

The oil palm industry in Malaysia started 80 years ago in a modest way. Today it is the largest in agricultural plantation sector, exceeding rubber plantation by more than double in area planted. In terms of hectare, the total area under oil palm cultivation is over 2.65 million hectares, producing over 8 million tones of oil annually (Pradeepkumar et. al., 2008). The oil consists of only 10% of the total biomass produced in the plantation. The remainder consists of huge amount of lignocelluloses materials such as oil palm fronds, trunks and empty fruit bunches. The projection figures of these residues are as follows (Pradeepkumar et. al., 2008):

- 7.0 million tones of oil palm trunks
- 26.2 million tones of oil palm fronds
- 23% of Empty Fruit Bunch (EFB) per tone of Fresh Fruit Bunch (FFB) processed in oil palm mill

Besides producing oils and fats, at present there is a continuous increasing interest concerning oil palm residues. Extraction of the oil from fresh oil palm fruit lets requires separation of the fruit lets from empty fruit bunches prior to further processing. These empty fruit bunches, which consist of fibers and shells, are often used as boiler fuel by palm oil mill plants to produce steam for electricity generation and palm oil extraction (Hashim and Chu, 2002). Each year, more than 100,000 tons of oil palm ash has been disposed and tended to increase annually. The ash produced after burning requires ultimate disposal. The use of ash particles derived from the combustion of agricultural wastes as zeolites would therefore be most ideal since these materials are inexpensive and available in abundance.

2.1.1 The Usage of Oil Palm Ash in Malaysia

Presently, oil palm ash (OPA) that obtained from incineration of empty fruit bunch can be used as a source of fertilizer due to its high potassium content. Some researches have utilized this OPA to synthesize absorbents for toxic gas removal (sulfur dioxide, SO_x) (Husin et.al., 2005). The active compound (silica, alumina, potassium, calcium, and hydrated water) in the absorbent prepared from OPA is believed to be responsible for the high absorption capacity of SO_x (Nor Fatiha et. al., 2005). Beside that, the feasibility of using the shell and fiber ash as a construction material is also applicable (Tay and Show, 1995). The workability of concrete blended with the shell and fiber ash is good, and setting times are well within the requirements of both America and British standards. That is why the abundance of agro waste from oil palm industries in Malaysia has inspired researcher to utilize the potential usage oil palm ash to produce value added product such as zeolites.

2.1.2 Source of Oil Palm Ash in Malaysia

In total, about 90 million metric tones of renewable biomass (trunks, fronds, shells, palm press fiber and the empty fruit bunch) are produced each year. With the prices of the crude petroleum and world’s demand for oils and fats escalating to an unprecedented height every other day, one hectare of oil palm plantation can produce about 50–70 tones of biomass residues (Salathong, 2007). For each bunch of the fresh palm fruit, approximately 21% of palm oil, 6–7% of palm kernels, 14–15% of palm fibers, 6–7% of palm shells and 23% of empty fruit bunches can be obtained (Dalimin, 1995). The potentiality is further strengthened and driven by the insight that oil constitutes only 10% of the palm production, while the rest 90% is the biomass (Yong et. al., 2007). In Malaysia alone, the potential oil palm ash production is designated at 4 million tones/year (Mohamed, 2005). Increasingly, with the price of the ash disposal cost (either in landfills or ash ponds) hitting as high as $5/tones in developing countries and $50/tones in developed countries, the urgency of transforming the residue into a more valuable end product has been promulgated (Anonymous, 2009).

2.1.3 Characteristic of Oil Palm Ash in Malaysia

Oil palm ash (OPA) is a by-product from burning process in palm oil plantation, which palm nut and fiber of palm are burnt at temperature about 800- 1000ºC**.** Typically, oil palm ash is characterized by a spongy and porous structure in nature, of which its main components are in the angular and irregular form, with a sizable fraction showing cellular textures (Chindaprasirt et. al., 2008). Meanwhile, raw palm ash was evidenced consist a rather spherical particle with a median size of 183.0 µm while medium and small particles ground palm ash were individually noted containing crushed shape structures with a median of 15.9 µm and 7.4 µm (Jaturapitakkul et. al., 2007).The main chemical composition of oil palm ash is silica which is have great similarities with the raw materials typically used in the manufacture of zeolites. The ash produced sometimes varies in tone of colour from whitish grey to darker shade based on the carbon content in it.

a) XRD analysis

XRD patterns reveal phase, chemical and crystalline structure information of oil palm ash. Figure 2.1 shows the example of XRD patterns of oil palm ash which indicate the qualitative presence of crystalline minerals. The diffraction intensities as reflected by corresponding counts per second were used as the indication of changes among the patterns of the ashes.

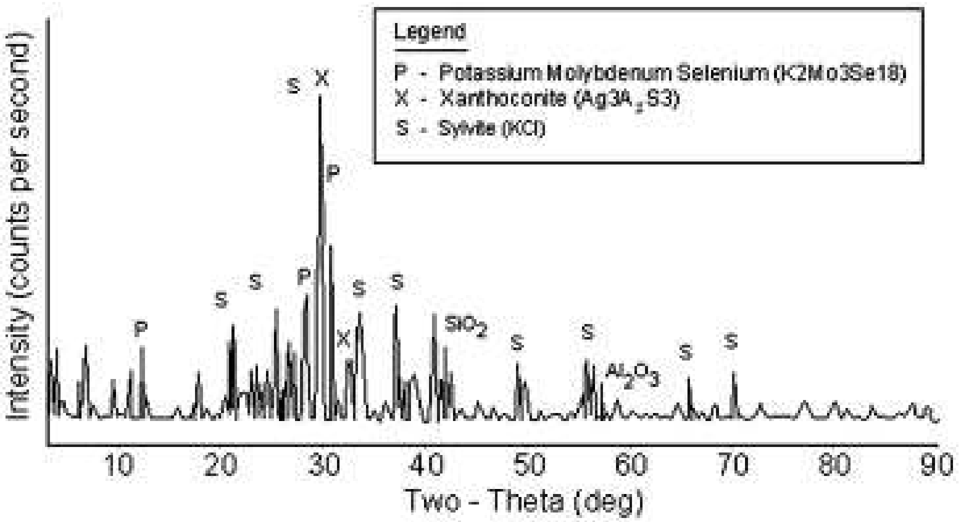

Figure 2.1: XRD pattern of oil palm ash

b) Morphological structure

Morphological structure of oil palm ash is determined using scanning electron microscope. Meanwhile, raw palm ash was evidenced consisting rather spherical particles with a median size of 183.0µm while medium and small particles ground palm ash were individually noted containing crushed shape structures with a median of 15.9 µm and 7.4 µm (Foo and Hameed, 2009).

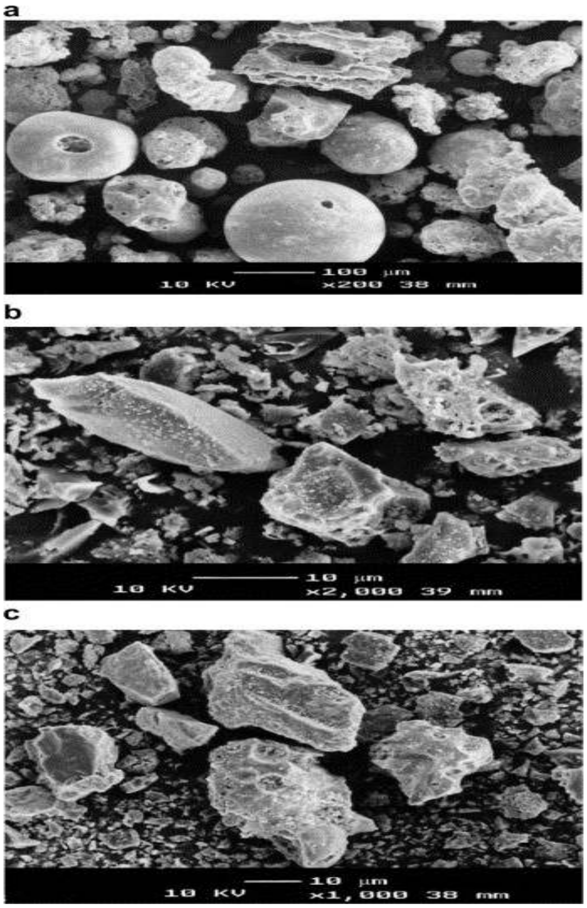

Figure 2.2: Scanning electron microscopy images of oil palm ash. (a) Large size particles of oil palm ash (LP) (b) Medium size particles of oil palm ash (MP) (c) Small size particles of oil palm ash (SP)

c) Chemical composition

Chemical composition of oil palm ash usually determined its quality. In most cases, the chemical elements of oil palm ash are found to be silicon dioxide, aluminium oxide, iron oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide and sulfur trioxide, fluctuating upon the varieties of proportion of irrigated area, geographical conditions, and fertilizers used, climatic variation, soil chemistry, timeliness of production and agronomic practices in the oil palm growth process (Awal and Hussein, 1997).

Table 2.1: Chemical Composition of Oil Palm Ash

Chemical composition of OPA	**Percentage (%)**
SiO_2	40.0
K_2O	12.1
CaO	10.0
P_2O_5	8.2
MgO	6.4
Al_2O_3	6.1
C	5.4
Fe_2O_3	2.5
Others	2.0
Ignition loss	7.3

2.1.4 Recycling of Oil Palm Ash

Oil palm industry has been one of the most successful stories of the world agricultural sector abroad the nations. Malaysia's palm oil industry leaves behind huge amount of biomass such as oil palm ash from its plantation and milling activity, way much larger as compared to other types of biomass. Therefore the oil palm ash from oil palm industry has potential to be converted to commercial products such as zeolites. Simultaneously, oil palm ash, an abundantly available throwaway waste from the fired-boiler furnaces, has currently emerged to be an ideal adsorbent in the wastewater treatment processes and as air purifier in cleaning of atmosphere contaminants. Nowadays, there is also variety of research covering the oil palm ash as a supplementary cementitious material in producing high-strength concrete. On the contrary, attempted the employment of oil palm ash as sludge chemical binders for stabilization of pH, reduction of contaminants mobility and improving of physical integrity via a combination of precipitation, encapsulation, chemisorptions and ion exchange processes (Chun et. al., 2008). In the natural rubber processing industry, the possibility of oil palm ash as coupling agents for remedying the compatibility of hydrophilic and hydrophobic polymer matrix while enhancing its hardness, stiffness, brittleness and vulcanization curing rates is determined by an extend research and experiment (Ismail and Haw, 2008).

2.2 Introduction to Natural Zeolites

Natural zeolites are hydrated aluminosilicates, comprising of hydrogen, oxygen, aluminium, and silicon arranged in an interconnecting, open, three-dimensional structure (Stead et. al., 2003). The primary building units are $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked together by oxygen atoms. Their crystal structure allows water molecules to be held and removed within the channels and cavities within the lattice. These cavities can also contain exchangeable cations, in particular K, Na, Mg, Ca, Sr and Ba. The cavities and channels that exist within the zeolites framework can constitute as much as 50% of the total crystal volume (Passaglia & Galli, 1991), whilst water constitutes as much as 10-20% by weight of the natural zeolites (Mumpton, 1983). The presence and occupation of cations, within the cavities and channels will largely rule the amount of water contained within the zeolites framework. The general empirical formula, which represents a zeolites chemical structure, is shown below:

$$M_{2n}O \,.\, Al_2O_3 \,.\, {}_xSiO_2 \,.\, {}_yH_2O$$

M represents any alkali or alkaline earth cation, n the valence of the cation, x varies between 2 and 10, and y varies between 2 and 7 (Hawkins, 1983), with structural cations comprising Si, Al and Fe^{3+}, and exchangeable cations K, Na and Ca. Natural zeolites are not found as pure minerals. They can often contain small percentages of quartz, feldspar, clay minerals, cristobalite, calcite, gypsum and untreated volcanic glass.

Natural zeolites were first discovered in 1756 by the Swedish mineralogist Freiherr Axel Fredrick Cronstedt (Mumpton, 1983). However, it was not until the late 1950s that researchers showed their effectiveness for environmental protection and remediation. With more than 2000 deposits found globally natural zeolites are a natural plentiful resource, and are inexpensive to mine, since the majority of deposits are found close to the earth's surface. Natural zeolites constitute more than 90% of many sedimentary rocks of volcanic origin (Hawkins, 1983). The production of synthetic zeolites began in the late 1800s for industrial use and is now perhaps better known as phosphate replacements in laundry detergents. Natural zeolites are less expensive than synthetic zeolites and as such are being increasingly used for agriculture, aquaculture, agronomy, animal husbandry, energy conservation, and wastewater treatment and pollution control (Stead et. al., 2003).

Zeolites also preferable known as "molecular sieves." The term molecular sieve refers to a particular property of these materials which is the ability to selectively sort molecules based primarily on a size exclusion process (Anonymous, 2010). This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels.

2.2.1 Structure and Classification of Zeolites

The original publication by Breck contains a clear presentation of zeolites structure (Breck, 1974). It is very instructive to compare his presentation of the material to the one given here. Higgins (1994) has an introduction to siliceous zeolites highly complementary to Gies review on clathrasils (silicates with voids but no pores) (Gies et. al., 1998). Information on the crystallography and nomenclature of zeolites can be found in the highly readable publications by McCusker (McCusker et. al., 2001).

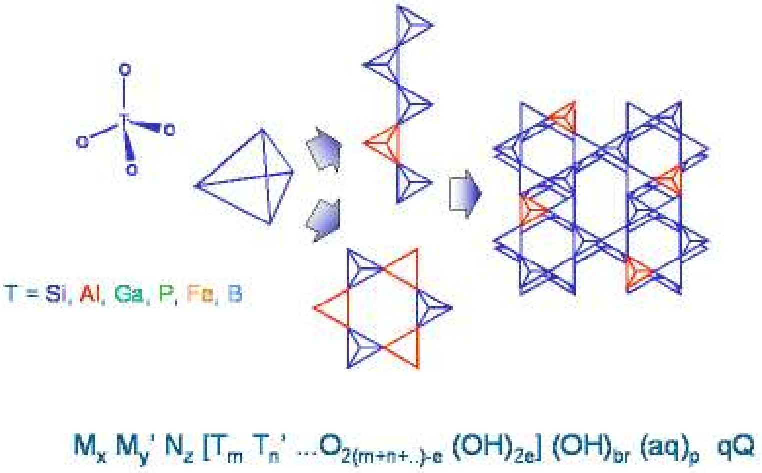

Figure 2.3: Several representations of the basic building unit of zeolites, the tetrahedral. These tetrahedral are connected via corners, thus forming the crystal structure of the specific zeolite.

Source: Atlas of Zeolite Framework Types, 2001.

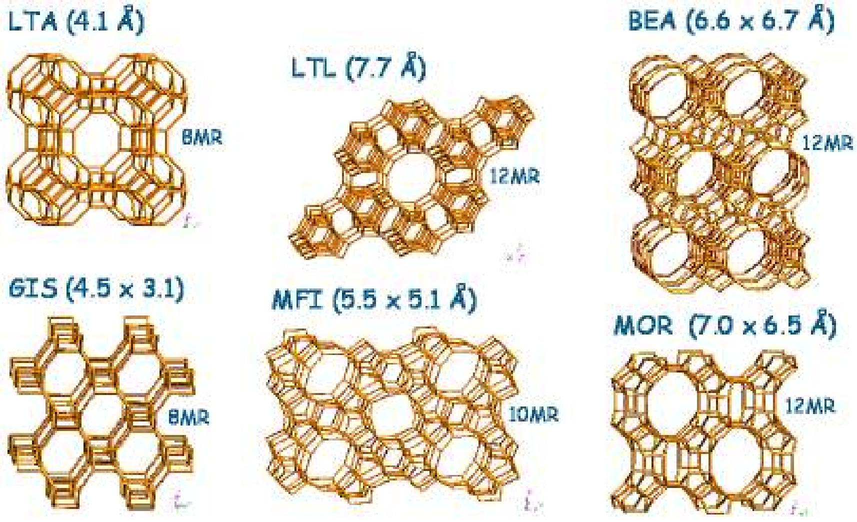

Figure 2.4: The number of tetrahedral forming these channels and/or windows are given beside the structures (LTA: Zeolite A, LTL: Zeolite L, BEA: Zeolite Beta, GIS: Gismondine, MFI: ZSM-5 (Zeolite Socony Mobile No. 5), MOR: Mordenite).Source: Atlas of Zeolite Framework Types, 2001.

The most recent Atlas of Zeolite Framework Types lists about 133 framework structures (Baerlocher, Meier and Holson, 2001). Liebau and co-workers have proposed a classification for porous tectosilicates that distinguished between aluminious (porolites) and a siliceous (porosils) framework as well as frameworks that do (zeolites/zeosils) and do not (clathralites/clathrasils) allow exchange of guest species, and are summarized in Table 2.2 (Liebau et. al., 1986). IUPAC recommendations for nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic host with particular attention to the chemical composition of both host and guest species, structure of the host, structure of the pore system and symmetry of the material have been published.

Table 2.2: Classification of Porous Tectosilicates

Porosils (SiO_2 based)		Porolites (aluminosilicates)	
Clatharasils	Zeosils	Clathralites	Zeolites
Silica sodalite	Silicalite	Sodalite	Faujasite
	Silica ZSM-22		Mordenite
			ZSM-5
Dedocasil	SSZ-24		Zeolite A

The Structure Commision of the International Zeolite Association identifies each framework with a three-letter mnemonic code. Table 2.3 lists the three-letter codes for open four-connected three dimensional (3D) framework types. Thus, the LTA framework encompasses zeolite A, as well as its ion-exchanged forms with K^+ (3A), Na^+ (4A), and Ca^{2+} (5A), frameworks α, Zk-6, N-A, and SAPO-42. Figure 2.5 provides details on some selected zeolite frameworks (Newsam et. al., 1992).