



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

Zeolite

Zeolite is one form of an alumino silicate crystal that was found by Axel Fredrik Cronstedt, Swedish mineralogist. In an easy way, we can think about the structure of zeolite in that it is a silicon oxide crystal in which some Si^{4+} is replaced by Al^{3+} . Zeolite is really attractive for commercial because it is cheap and it has really effective properties in being absorbent, cation exchanger, and catalyst.

2.1 Zeolite's Properties

Zeolite has four wonderful properties that are really attractive for commercialize and researching.

2.1.1 Adsorbent

Zeolite can be used as an adsorbent because it is a porous material. So the particle that is smaller than the pore size can be adsorbed and stay in the pore.

2.1.2 Cation Exchanger

Due to the negative charge on the surface of zeolite, they can adsorb a metal ion on their surface. Some type of cation is an exchangeable ion for example Na^+ ion, so zeolite can exchange the cation on the surface with the ion in the surrounding.

2.1.3 Catalytic Ability

Zeolite can be used as a catalyst due to its specific site adsorption ability and its silica framework. It can adsorb proton and make that site be more acidic. The silica structure make zeolite tolerate high degree of heat. So it can be used a catalyst that need an acidic catalyst in a wide range of heat.

2.1.4 Shape Selection

When zeolite adsorbs particle, it will adsorb only those fit the pore and exclude a too large molecule. This way zeolite acts as a molecular sieve. Furthermore, by adding a steric constraint into the pore, the adsorption will be more selective on size and shape of the molecule. So, we can use zeolite as a shape selective material as well.

2.2 Zeolite's Structure

All fascinating properties of the zeolite can be determined by studying a structure of the zeolite. For example, zeolite's sorption ability is dependent on the size and number of the pore. Zeolite's exchange capability is dependent on the Al/Si ratio in which tells the amount of ion that zeolite can carry. So it is necessary to study about crystal structure of zeolite including a composition of them.

2.2.1 Characteristic of Zeolite Framework Types.

One feature that all zeolites have in common is they share the same 3-D and 4-connected framework structure constructed from corner-sharing TO₄ tetrahedral, where T is any tetrahedrally coordinated cation. A description of the zeolite structure is usually described in the characteristic of the size of the pore openings and the dimensionality of the channel system. The size of pore opening is usually dependent on the size of the ring in the crystal. Furthermore the size of the ring is determined by T atom a corner cation in the crystal. For example, in an 8-ring which is considered as a small pore, 10-ring which is medium, and a 12-ring which is a biggest size of all three sizes of ring, they have an diameter as 4.1, 5.5 and 7.4 angstrom respectively. At present there are a hundred of the confirmed zeolite framework types.

Even now there are over 133 types of zeolite crystal type, only a few of them describe zeolites or zeolite-like materials that are actually used in industrial application. The fifteen types below are the example of those selected.

2.2.1.1 LTA (Zeolite A)

This framework consists of primitive cubic arrangement of alpha cage joined through single 8-rings. This kind of crystal is considered as a zeolite A. It is used as a desiccant in the laboratory glass ware and between the panes of glass in double-glazed windows.

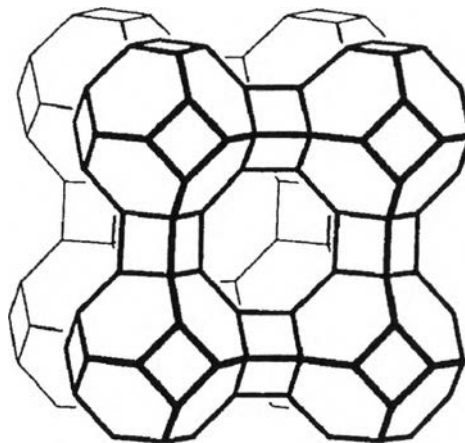


Figure 2.1 LTA framework.

2.2.1.2 CHA (Chabasite)

This kind of framework is a member of the ABC-6 family of zeolite framework. CHA has an ABC stacking of double 6-ring arrays. This stacking produces an elongated cage with six 8-ring pores and a 3-dimensional channel system. However, the channel in CHA are not straight. This framework is suited for a conversion of methanol to olefins and in the aldol condensation of aldehyde.

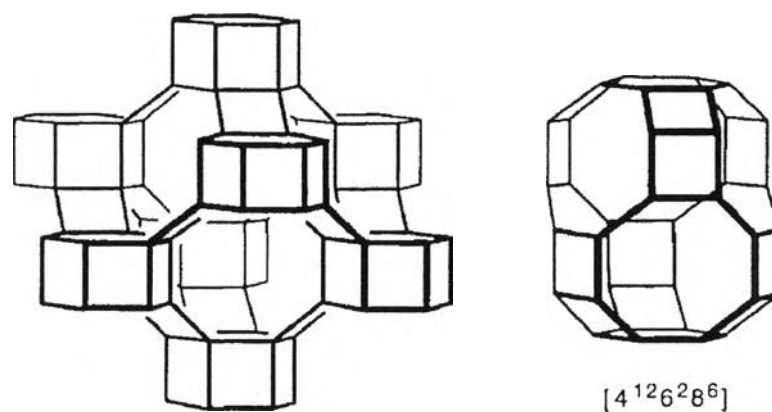


Figure 2.2 CHA framework.

2.2.1.3 GIS (gismondine)

This framework can describe as a stacking of 2-dimensional arrays of double crankshaft chains. There are 8-ring channels in the parallel to x and y. Those channels are displaced with respect to z-axis. From the intersection, they form a 3-dimensional channel system. GIS is suitable for being an ion exchanger in detergents.

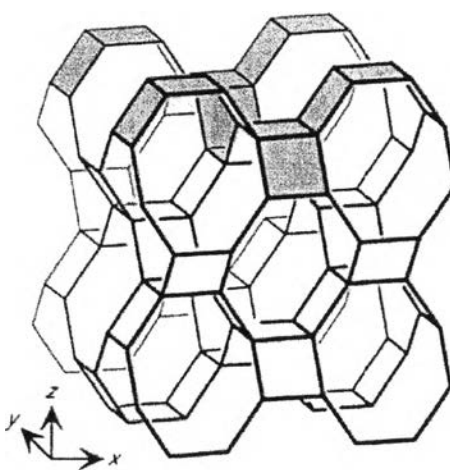


Figure 2.3 GIS framework.

2.2.1.4 MFI (ZSM-5)

ZSM-5 can be described as a group of pentasil unit (eight units of 5-ring structure). Pentasil unit are linked together via an oxygen bridges to form corrugated sheets with 10-ring holes. Each sheet is linked by oxygen bridges to the next to form the 3-dimensional structure. Adjacent sheets are related to one another by an inversion center. This produces straight 10-ring channels parallel to the corrugations (along y), and sinusoidal 10-ring channels perpendicular to the sheets (along x). The latter channels link the straight channels to one another to form a 3-dimensional 10-ring channel system. ZSM-5 has found many applications in refinery and petrochemical processes.

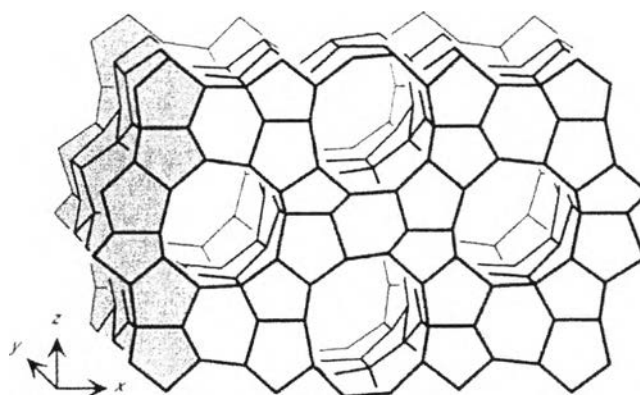


Figure 2.4 ZSM-5 framework.

2.2.1.5 MEL (ZSM-11)

In this framework, it has the corrugated sheets of pentasil chains that are in the ZSM-5 are also present.

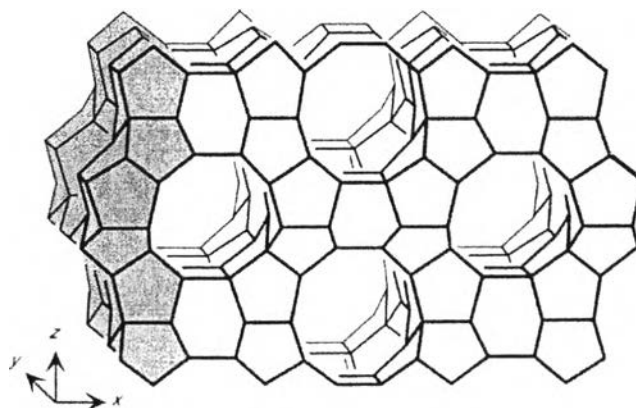


Figure 2.5 ZSM-11 framework.

2.2.2 Zeolite's Application and Modification

2.2.2.1 *Zeolite as an Adsorbent*

Velu S. et al (2003) researched about the ability to remove sulfur from jet fuel by using zeolite-based adsorbent. Before they used material, they modified the material by exchanging various ions (Cu^{2+} , Ni^{2+} , into zeolite. They founded that the Ce-zeolite exhibited a good sulfur adsorption. The capacity of the adsorption is about 10 mg/g of adsorbent.

2.2.2.2 *Zeolite as a Catalyst*

Panagiotis G. et al modified the beta zeolite with H_2PtCl_6 impregnation for a catalyst in reforming reaction. They could transform aromatic and cyclic saturated multibracned molecules to higher octane number species.

2.2.2.3 *Zeolite as an Ion Exchanger*

From Milan Z., (1997), they reported about the ammonia removal by exchanging with the homoionic zeolite. They used K-zeolite, Mg-zeolite, Na-zeolite, and Ca-zeolite. The result showed that Na-zeolite is the best exchanger. It removed

2.2.2.4 Antibacterial Zeolite

Due to remarkable properties of zeolite, they are being used in many applications. One of the most interesting applications is antibacterial zeolite. There are many approaches that have been using to modify zeolite to be an antibacterial material.

Matsumura Y. et al said that zeolite impregnated with Ag can inhibit the growth of bacteria (*Escherichia coli*) at the comparable level to the silver nitrate solution both in an anaerobic system and an aerobic condition.

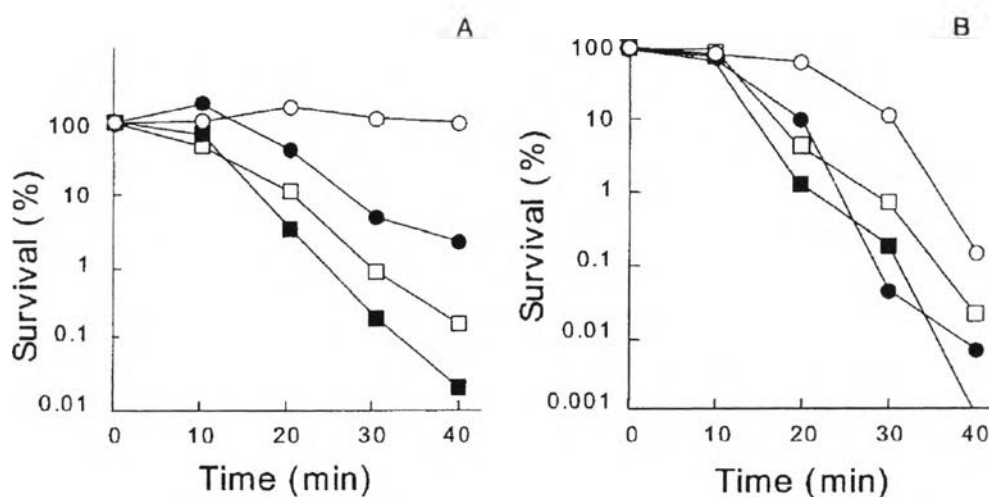


Figure 2.6 Bactericidal activities of silver zeolite and silver nitrate in anaerobiosis and aerobiosis cells were treated at 37°C with silver zeolite at 10 mg/ml in 20 mM potassium phosphate buffer (circles) or silver nitrate at 1 μ M in 20 mM HEPES-NaOH buffer (squares) anaerobically (open symbols) or aerobically (closed symbols).

Furthermore they suggested two mechanisms of an antibacterial action of silver-zeolite. First, in order to inhibit bacteria growth, silver ion need to contact with the bacteria directly. Second, silver ions in zeolite produce an active oxygen species from the respiratory inhibition process of silver toward bacteria.

(M. Hotta et al, 1998) they did experiment on Ag-Zn-zeolite in order to study the antibacterial activity at various ratio of Ag and Zn. They tested on four types of bacteria (*Streptococcus mutans*, *Streptococcus mitis*, *Streptococcus salivarius*, *Streptococcus sanguis*). They founded that there is no difference in growth inhibition while increasing the amount of Ag and Zn ion released from zeolite. Furthermore, they mixed zeolite with urethane acrylate-based resin in order to use it as a filling material in dentistry.

Azben T. and Semra Ü. (2003), they reported that the selectivity of the exchanger level of Ag^+ compared with Na^+ , Zn^{2+} and Cu^{2+} in Na-clinoptilolite (one form of zeolite) is in the trend like $\text{Ag}^+ > \text{Na}^+ > \text{Zn}^{2+} > \text{Cu}^{2+}$. They calculated the equivalent fraction of the ingoing ion in the solution (A_s) against that in the solid phase (A_z) by using the equations below.

In addition, they tested the antimicrobial activity of them and plotted the diameter of inhibition zone against A_z of the three ions. They founded that silver is the strongest bacteria growth inhibitor. However, higher exchanger level does not affect the size of the inhibition zone.

Fox S. et al. (2010) reported a production of NO-loaded Zn^{2+} -exchange zeolite material for antibacterial and other clinical applications. As a result, The antibacterial properties of NO- releasing zeolites against gram-negative *Pseudomonas aeruginosa* and gram-positive methicillin-sensitive and methicillin-resistant *Staphylococcus aureus* showed a potential to inhibit bacterial growth.

Y. Zhou et al. (2003) showed an antimicrobial of Cu^{2+} -montmorillonite against *E. coli* and *S. faecalis* bacteria. They found that the minimal inhibitory concentration (MIC) and killing concentration of Cu^{2+} -montmorillonite on those bacteria were ~10 and ~50 ppm, respectively. However, the ability of this antimicrobial clay is not better than that of Ag^+ -zeolite.

Haile T. et al. (2008) reported an ability of silver-zeolite to inhibit corrosion caused by bacteria. The evaluation was performed by the amount of leaching Ca^{2+} and Si^{4+} from the cementitious matrix, rate of bacterial sulphur oxidation,

increase in biomass concentration, and acid production. The cumulative concentration of calcium ion leaching were 3.5-folds higher and 2-folds higher in the uncoated and epoxy coated mortar specimens compared to those of zeolite coated specimen. The cumulative leaching silicon ion was also 2.6-folds higher in the control mortar specimens. Biomass concentration in the control reached 210 mg TSS/L, and that of the zeolites coated mortar was 103 mg TSS/L. The bacterial sulphur oxidation was found to follow the same pattern of the bacterial concentration of 230-270 mg SO₄/g S and 158-182 mg SO₄/g S in the control and zeolite coated mortar specimens, respectively. The resistance of the zeolite coating was further evidenced by increase in pH of the control mortar specimens which demonstrated the leaching of gypsum (Ca(OH)₂) from the cement matrix. The stability of zeolite coated specimen was also confirmed by the lack of corrosion product examined by FE-SEM and XRD results.

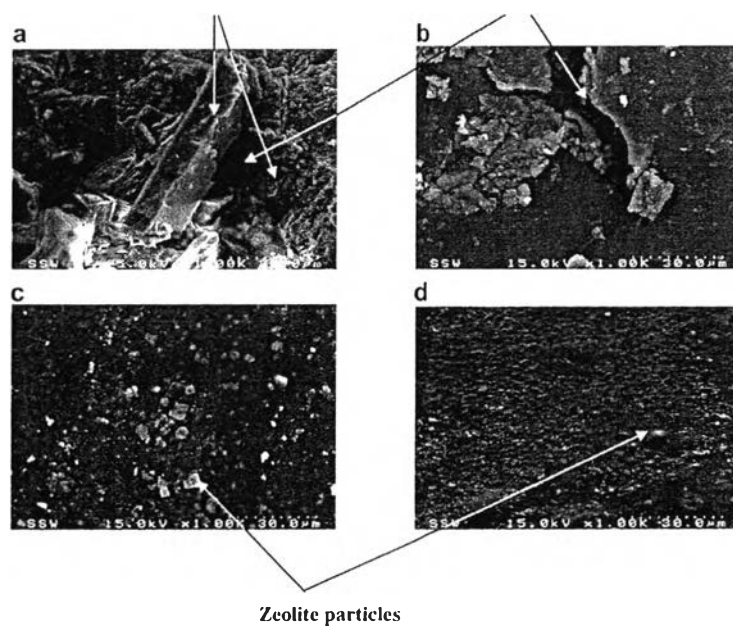


Figure 2.7 Scanning electron micrographs of mortars (A) uncoated, (B) epoxy coated, (C) type AC antimicrobial zeolite coated, and (d) type AK antimicrobial.

Bright et al (2007) did their research on synthesis of zeolite x and loaded Ag by ion exchange. Their purpose was to use the material in antibacterial action. As a result Synthesized zeolite x can load Ag^+ at 2.0 %w/w in the crystal and 5.8 %w/w on the surface. *Escherichia coli* and *Pseudomonas aeruginosa* and *Staphylococcus aureus* suspended in soya broth were exposed to 0.15, 0.25, 0.5 and 1.0 g/L of material for 24 hours. In one hour, there is no viable cell of bacteria survived.

Narin G. et al (2010) reported the antibacterial activity of nitric oxide releasing natural zeolite. They reported the result that zeolite itself has no any antibacterial action. The antibacterial capability was occurred after loading with NO by purging NO at the rate of 20 ml/min for 12 hours.

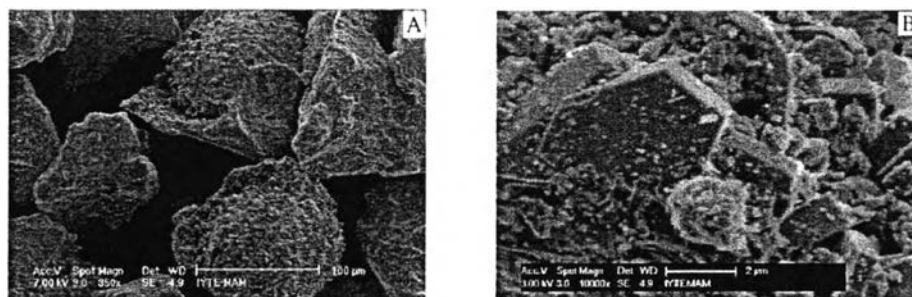


Figure 2.8 SEM micrograph of NZ (scale bar are 100 micron and 2 micron for A and B).

After treating a supernatant got from treating material with PBS buffer with a gram positive *Bacillus subtilis* and gram positive *Escherichia coli*, it showed a completely eradication of the bacteria cell at 7.5 mg/ml and 12.5 mg/ml of zeolite concentration in PBS respectively.

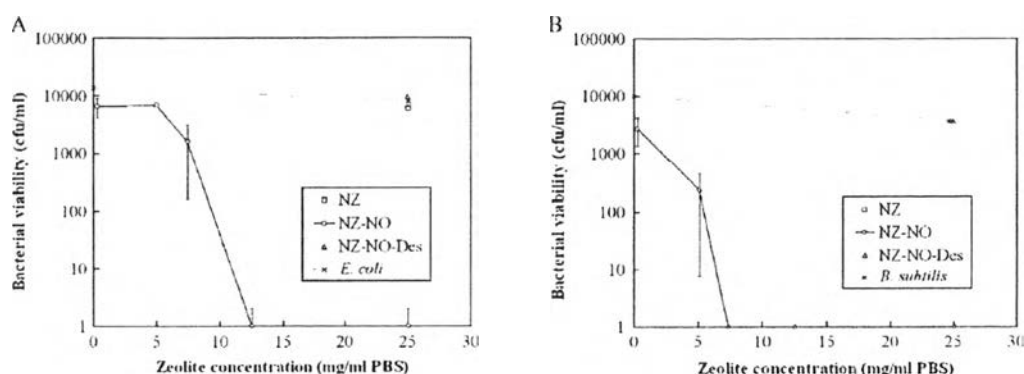


Figure 2.9 Bactericidal activity of NZ-NO in PBS pH 7.4 37 °C against (A) *E. coli* and (B) *B. subtilis*.

Galeano B. et al (2003) studied the antibacterial action of Ag-Zn-zeolite coated on stainless coupons. They coated Ag-Zn-zeolite containing 2.5% (w/w) silver and 14% (w/w) zinc and was applied onto a substrate for 0.5 mm of thickness. They tested with three Bacillus spp. (*B. anthracis* Sterne, *B. cereus* T, *B. subtilis* 168) in the interval of 0, 2, 6, 12, 24, or 48 hours. They found that within 24 hours all bacteria cell is reduced for 99%. However, dormant spores are resistant to silver-zinc zeolites owing to the high resistance to ROS conferred by spore coat layers (Riesenman *et al.*, 2000).

Gabriek Cik et al (2001) reported about the zeolite (ZSM-5) modification by exchanging the Na^+ with Cu^{2+} . After that they synthesized the Cu(II)-complexes of thiophene via oxidative polymerization reaction. They tested a biological activity of the material with microscopic fungi (*A. niger*, *C. albicans*), bacteria (gram negative *E. coli*, gram positive *S. aureus*). In testing with fungi, material seemed to enhance a sporulation process and involved in killing of yeast. Furthermore, sporulation enhancement was influenced by the thiophene oligomers in the biochemical process, in which they can function as an organic carbon reservoir. Despite of the thiophene involvement, the killing of cell was caused by the releasing of Cu ion into the medium. In bacteria testing, the percentage of killed cell was increased under the coactions of

light. Sothey concluded the light effect attributed to the photogeneration of reactive oxygen species (hydroxide radical), which can be produced either in the material or on the surface of the zeolite.