

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Fly Ash

The fly ash produced from the burning of pulverized coal in a coal-fire, boiler is a fine-grained, particulate material carried off in the flue gas. It is usually collected from the flue gas by means of electrostatic precipitation, bughouses, or mechanical collection devices such as cyclones.

Fly ash may be sub-divided in two categories, according to their origins:

1. Fly ash normally produced by burning anthracite or bituminous coal
2. Fly ash normally produced by burning lignite or sub bituminous coal.

Lignite is characterized by higher concentration of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as a lower carbon content, compared with bituminous coal fly ash. Very little anthracite coal is burned in utility boilers, so there are only small amount of anthracite coal fly ash

2.2 Chemical composition of fly ash

The chemical and mineralogical composition of fly ashes depends upon the characteristics and composition of coal burnt in the power plant. Fly ashes are composed mainly of mineral matter in the form of glassy particles (50-90%). A small amount of ash occurs in the form of crystals. Unburned coal is collected with the fly ash particle of carbon, which may constitute up 16% of the total weight, depending on the rate and temperature of combustion [Turatum, 2001] the degree of pulverization of the original coal, the fuel/air ratio, the nature of the coal being burned, etc.

Major minerals found in fly ash include:

- Silica (SiO_2) 41-58% by weight
- Alumina (Al_2O_3) 21-27% by weight
- Iron oxide (Fe_2O_3) 4-17% by weight
- Lime (CaO) 4-6% by weight
- Other minerals, e.g. MgO , SO_3 , Na_2O and K_2O , etc.

2.3 Zeolite

Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations [Sopontammakorn, 2001] water and/or other molecules within their pores. Many occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic, and are made commercially for specific uses, or produced for research purposes.

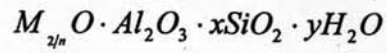
Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tones per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as *molecular sieves*.

Zeolites are actually natural products. However, not all naturally occurring zeolites have been recreated in the laboratory, and vice versa, many zeolites have been synthesized that do not occur in nature.

Mineral or naturally zeolite is a crystal of amino silicate group of mono or divalent base which mostly find in ore-mining. Partially or full lost of water can occur during the process of crystallization, but the crystal structure remains the same. Mineral Zeolite's samples are faujasite, erionite, offrite, chabazite, gmelinite, mordenite, heulandite etc.[Tongkam, 1999]

Synthetic zeolites occur from a source of alumina, silica and alkali such as NaOH. The synthesis can occur in gelation form, porous form and sandlike form. Alumina and silica of zeolite are a crystal of amino silicate which has alkaline's water of crystallization or alkali earth that mostly are Na, K, Mg, Ca, Sr and Ba. The structure of zeolite can be classified into primary and secondary unit. Primary unit is the structure of the zeolite which consists of a three-dimensional framework of SiO_4 and AlO_4 tetrahedral as present in Figure 2.1. Each of which contains a silicon or aluminum atom in the center. And secondary unit is composed two primary unit such as ZSM-5, ZSM-11, Faujasite, etc

Zeolites may be represented by the empirical structure as:



Or by a structural formula

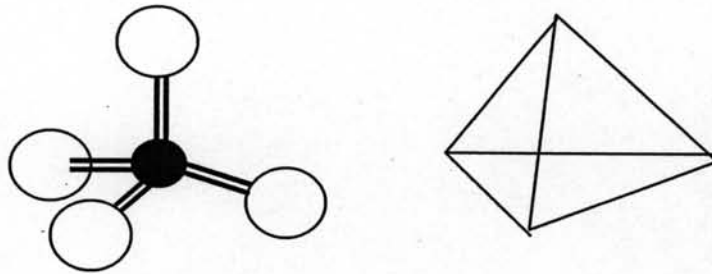
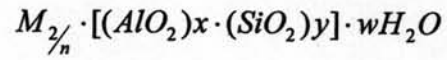


Figure 2.1 primary building units

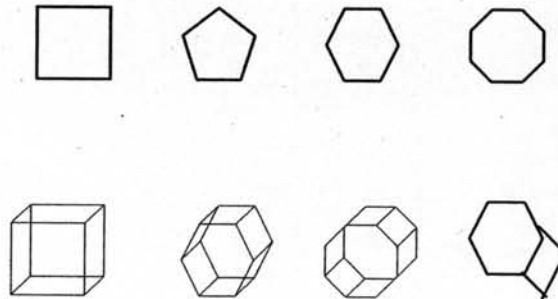


Figure 2.2 secondary building units

2.4 Applications of zeolite

2.4.1 Catalyst

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reaction is that catalyzed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. Examples are the use of titanium ZSM-5 in the production of caprolactam, and copper zeolite in NO_x decomposition.

2.4.2 Adsorption and Separation

The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability to adsorb certain molecules while excluding others, has opened up a wide range of molecular sieving application.

2.4.3 Ion Exchange

High cation exchange capacity of zeolites allows them to be used as resin for exchanging cations of divalent

Factor of ion exchange

- nature of cation
- temperature
- concentration of cation in solution
- type of anion mix with cation in solution
- Solvent
- Structure of zeolite.

2.5 Synthesis of zeolite

There are two main methods for the synthesis of zeolite: (i) hydrothermal, and (ii) fusion methods. Hydrothermal method is generally milder but takes much longer time than the fusion method. In addition, the formation of zeolite crystal is usually interfered by the formation of secondary phase. A less popular fusion method is a synthesized process between the mixture of alumina (e.g. sodium aluminate or

aluminium sulfate), silica (e.g. silica sol, fumed silica, or sodium water glass), and an alkali such as NaOH. The merit of this fusion method is that the resulting zeolite is more likely to be a highly crystallinity and the time required for the process is generally much shorter than the hydrothermal synthesis. The properties of final zeolite product depend on a complex interaction between many variables including $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the starting medium, fusion temperature, pH, water content, aging, stirring, and the presence of various inorganic and organic cations. Much remains to be learnt about how the initial reaction mixture forms the precursor species and how these arrange into the final crystalline products. A key concept is that the cations presented give rise to a templating action, but clearly the process is more complex.

2.6 Literature review

As stated earlier, the properties of zeolite can be manipulated by varying several formation parameters. For adsorption applications, one of the most significant properties of the fly ash is the cation exchange capacity (CEC) or cation binding capacity (CBC). This property is generally controlled by the level of crystallization in the zeolite structure which is, in turn, a function of the conditions during the preparation. In this section, only the fusion method is considered as it is often reported to yield the product with higher CEC than the hydrothermal product. The fusion method can be diagrammatically shown in Figure 2.3.

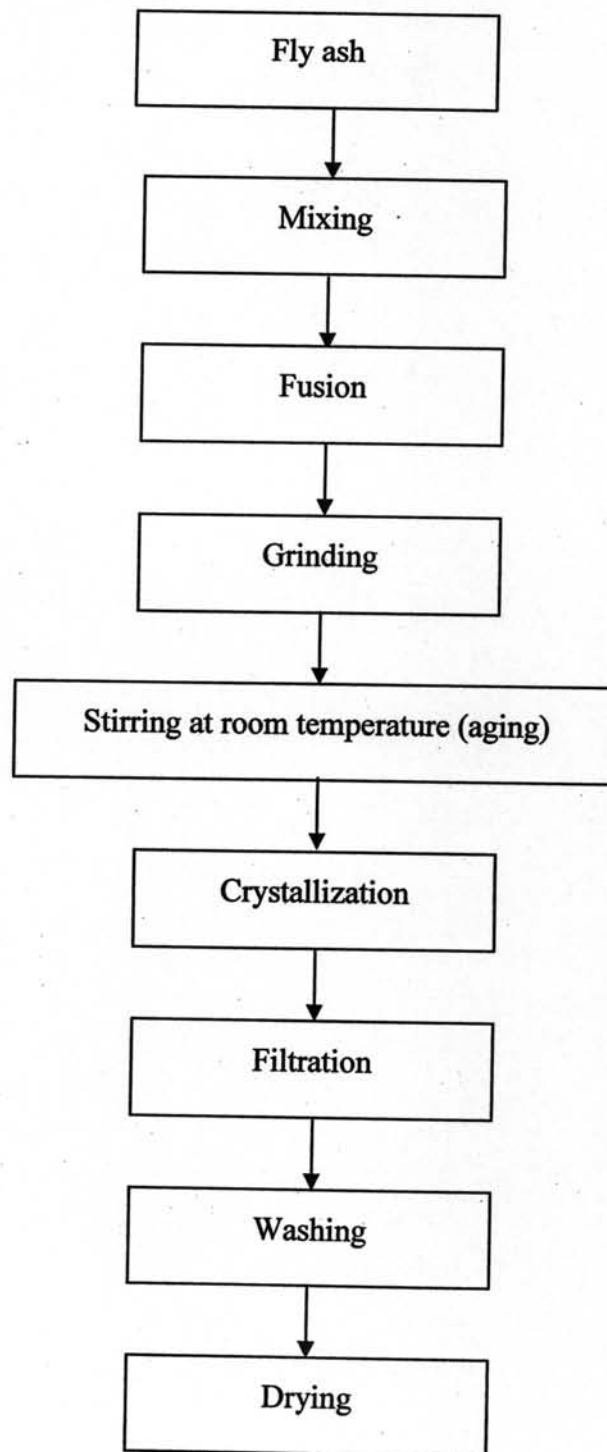


Figure 2.3 Steps in the fusion method

Figure 2.3 illustrates that the fusion method consists of four main steps, i.e. mixing fly ash with NaOH, fusion, crystallization, and final washing/drying. The condition of each step can significantly alter the properties of the final product. Literature regarding the effect of the various parameters on the CEC/CBC properties of the zeolite can be summarized as follows.

Table 2.1 demonstrates the effect of the ratio of activated reagent (e.g. NaOH) and the fly ash where an increase in NaOH content would lead to an increase in % crystallinity and also the CEC. This was due to the higher degree of zeolization taking place as a result of an increase in supersaturation obtained from a higher proportion of soluble species. However, there seemed to be the optimal ratio above which the properties of the zeolite deteriorated (Shigemoto et al., 1993). The fusion temperature is also an important factor for the formation of zeolite. Table 2.2 shows that there was an increasing trend in CEC when the fusion temperature increased. Similarly to the effect of NaOH content, a much too high temperature exhibited negative effect on the properties of the zeolite. Vaughan (1995) explained that, at this high temperature, iron bearing components in the fly ash could be decomposed during the fusion, and could then be incorporated into framework of the zeolite. This subsequently limited the crystallization process.

Another factor that influences the properties of zeolite is the crystallization temperature. This temperature was reported to affect the particle size of the resulting zeolite (see Table 2.3). This large particle size exhibited a higher CEC property, and therefore a higher temperature of crystallization led to a better CEC property. However, there is only few investigation on this aspect and so far there was no report on the effect of crystallization temperature higher than 90°C which is perhaps due to the high evaporation loss at the temperature closed to the boiling point of water. The crystallization time could also affect the CEC properties. The summary in Table 2.4 illustrates that a higher crystallization time could lead to zeolite with higher CEC. However, Molina and Poole (2004) reported that the crystallization could be adversely affected by the much too long crystallization time. This was reported to be due to the transformation of zeolite to a more stable structure. In fact, Molina and Poole (2004) demonstrated that different types of zeolite were formed at different crystallization time, from a less stable to a more stable type. However, there was no report relating the stability of zeolite with CEC properties in this work.

Table 2.1 Effect of ratio of activation reagent

| Activated reagent | Ratio activated Reagent | CEC (meq/100g) | CBC (meq/100g) | % Crystallinity | Crystallinity | Type of zeolite | References |
|-------------------|-------------------------|----------------|----------------|-----------------|-----------------------|-----------------|--------------------------|
| NaOH | 8 | | 160 | | Amorphous phases | Zeolite Y | Rayalu et al, (2000) |
| | 16 | | 260 | | Partially crystalline | Zeolite Y | |
| | 24 | | 420 | | Fully crystalline | Zeolite Y | |
| | 32 | | 340 | | Fully crystalline | Zeolite Y | |
| | 40 | | 240 | | Partially crystalline | Zeolite Y | |
| NaOH | 10 | 100 | | | | Zeolite x | Molina and Poole, (2004) |
| | 12 | 250 | | | | Zeolite x | |
| | 14 | 230 | | | | Zeolite HS | |
| | 16 | 200 | | | | Zeolite HS | |
| | 20 | 100 | | | | Zeolite HS | |
| NaOH | 11 | | | | | No zeolite | Somerset et al, (2005) |
| | 12 | | | | | Zeolite A | |
| | 15 | | | | | Zeolite A | |

| Activated reagent | Ratio activated Reagent | CEC (meq/100g) | CBC (meq/100g) | % Crystallinity | Crystallinity | Type of zeolite | References |
|-------------------|-------------------------|----------------|----------------|-----------------|---------------|-----------------|--------------------|
| NaOH | 1 | | | 10 | | Na-X zeolite | Okha et al, (2004) |
| | 1.25 | | | 70 | | Na-X zeolite | |
| | 1.3 | | | 80 | | Na-X zeolite | |
| | 1.5 | | | 30 | | Na-X zeolite | |

* CEC = Cation Exchange Capacity

** CBC = Cation Binding Capacit

Table 2.2 Effect of fusion temperature

| Range of fusion temperature | Fusion temperature (°C) | CEC* (meq/100g) | CBC** (meq/100g) | Adsorption | Crystallinity | Type of zeolite | References |
|-----------------------------|-------------------------|-----------------|------------------|---|----------------------|-----------------|----------------------|
| 200 – 800 | 200 | | 160 | | formation negligible | zeolite Y | Ruyalu et al, (2000) |
| | 600 | - | 420 | - | fully crystalline | zeolite Y | |
| | 800 | | 220 | | fully crystalline | zeolite Y | |
| 100-550 | 100 | | | Methyleneblue=22% Crystal violet=80% | | | Li et al, (2006) |
| | 200-250 | - | - | Methyleneblue=75% Crystal violet=90% | | | |

Table 2.3 Effect of crystallization temperature

| Range of crystallization temperature (°C) | Crystallization temperature (°C) | CEC (meq/100g) | CBC (meq/100g) | Adsorption | Crystallinity | Type of zeolite | References |
|---|----------------------------------|----------------|----------------|------------|-----------------------|-----------------|-------------------------|
| 40 - 90 | 40 | 130 | | | no crystallinity | zeolite x | Molina and Pool, (2004) |
| | 60 | 175 | | | little crystallinity | zeolite x | |
| | 90 | 250 | | | maximum crystallinity | zeolite x | |

Table 2.4 Effect of crystallization time

| Range of crystallization time (H) | Crystallization time (H) | CEC (meq/100g) | CBC (meq/100g) | Adsorption | Crystallinity | Type of zeolite | References |
|-----------------------------------|--------------------------|----------------|----------------|------------|-----------------------|-----------------|-------------------------|
| 3 - 3.5 | 3 | 300 | | | | zeolite A | Ruyalu et al, (2001) |
| | 3.5 | 430 | | | | zeolite A | |
| 0.5 - 6 | 0.5 | | | | no crystallinity | no zeolite | Molina and Pool, (2004) |
| | 1 | | | | little crystallinity | zeolite x | |
| | 2 | | | | maximum crystallinity | zeolite x | |
| | 6 | | | | little crystallinity | zeolite x, p | |