



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Poly(3-thiopheneacetic acid) (P3TAA)

A chemically cross-linked and water-swollen poly(3-thiopheneacetic acid)(P3TAA) gel was synthesized by Chen *et al.* [2000], and its swelling and spectral changes concern with their ionization were studied. The gel underwent an abrupt red shift in the electric spectra at certain pH, suggesting that a conformational transition due to ionization occurred despite the chemical cross-linkage. By changing the solvent composition, during the cross-linking, gels with an enhanced  $\pi$  conjugated structure was prepared. By doping of P3TAA gel with a  $\text{HClO}_4$  solution, a high electrical conductivity was obtained.

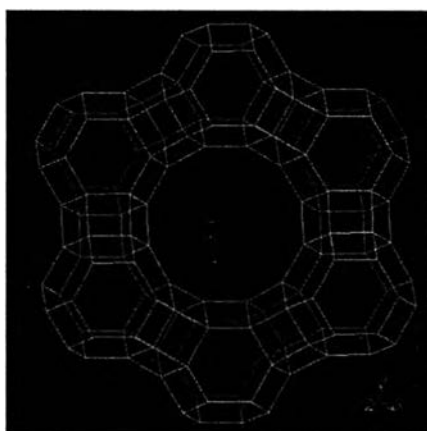
Chotpattananont *et al.* (2004) investigated the electrorheological (ER) of poly(3-thiopheneacetic acid) (PTAA), doped with perchloric acid ( $\text{HClO}_4$ ). The PTAA-based ER fluids showed the viscoelastic behavior under an applied electric field and the ER response was amplified with increasing electric field strength. The dynamic moduli,  $G'$  and  $G''$ , increased dramatically by ten orders of magnitude when the field strength was increased to 2 kV/mm. The suspensions exhibited a transition from fluid-like to solid-like behavior as the field strength increased, and reached a saturated ER response at a field strength of 1 kV/mm. Increasing particle concentration and particle conductivity resulted in a lower transition field strength.

Later the creep response of poly(3-thiopheneacetic acid) (PTAA) particles doped with perchloric acid were investigated by Chotpattananont *et al.* (2006). The increase in electric field strength at a fixed particle concentration and a fixed applied stress, the viscoplastic response diminished, and more elastic behavior ensued. For highly doped samples, at high-electric field strengths, the field-induced formation of thick fibrillar aggregates spanned the gap between the electrodes, each consisting of bundles of particle strings. The net effect of an increase of the electric field strength, particle concentration, or particle conductivity was to increase elasticity because of predominantly creation of fully connected particle strings.

The composites that were fabricated from Pth and zeolites, zeolites L (L), mordenite (MOR), and beta (BEA) were investigated by Thuwachaowsoan *et al.*, 2007. The electrical conductivity response toward H<sub>2</sub> was studied for the effects of zeolite contents, zeolite type, cation type, and cation concentration.

## 2.2 Zeolites

Zeolite structures are composed of tetrahedral Si(Al)O<sub>4</sub> units covalently joined by bridging O atoms to produce over 150 different types of framework. For example, FAU type zeolite has three dimensional 0.74 nm channels with 12 oxygen ring windows and supercages of 1-2 nm of diameter (Figure 1). It is inorganic porous material with a highly regular structure of channels and pores that allow some molecules to pass through, and cause others to be either excluded, or broken down, zeolites are used for very fine filtration. One might consider them to be precursors in current materials science research as nanotubes. The advantage of zeolite compared to other materials is that it ensures great effective surface, on which cations can be arranged by adsorption, intercalation or cation exchange reaction. Moreover, due to its thermal stability, shape selectivity and high acidity, it has been used as solid acid catalyst in many chemical reactions, such as isopropylation of benzene, and cracking of palm oil.



**Figure 2.1** The FAU type zeolite supercage (view along [111]) (Xu *et al.*, 2006).

Zeolite Y exhibits the FAU (faujasite) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes similar to LTA, and is made of secondary building units 4, 6, and 6-6. The pore diameter is large at 7.4Å since the aperture is defined by a 12 member oxygen ring, and leads into a larger cavity of diameter 12Å. The cavity is surrounded by ten sodalite cages (truncated octahedra) connected on their hexagonal faces. The unit cell is cubic ( $a = 24.7\text{Å}$ ) with Fd-3m symmetry. Zeolite Y has a void volume fraction of 0.48, with a Si/Al ratio of 2.43. It thermally decomposes at 793°C (Bhatia *et al.*, 1990).

The most important use of zeolite Y is as a cracking catalyst. It is used in acidic form in petroleum refinery catalytic cracking units to increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffins into gasoline grade naphthas. Zeolite Y has superseded zeolite X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio. It is also used in the hydrocracking units as a platinum/palladium support to increase aromatic content of reformulated refinery products (Ribeiro *et al.*, 1984).

Both microcrystalline and macrocrystalline beta samples were studied about the influence of the crystal size on the pretreatments. The catalytic activity of zeolite beta in the stereoselective Meerwein–Ponndorf–Verley reduction of ketones using secondary alcohols as reductant can be tuned by an appropriate pretreatment. During activation, water is essential to obtain an active catalyst. The formation of the initial catalytic site from the precursor is thought to be a lattice-attached aluminum-isopropoxide species; its formation can be easily reversed when water is present in the reaction mixture, thus the sensitivity of the reaction toward water (Kunkeler *et al.*, 1998).

The zeolite with its cavity structure, in which pores, channels, and cages of different dimensions and shapes are included, can ensure the accommodation and neutralization of a great number of Mg cations passing through the gel electrolyte during the performance of the cell. The advantages of zeolite compared to other materials are that it ensures great effective surface, on which cations can be arranged by adsorption, intercalation, or cation exchange reaction (Dalas *et al.*, 2004).

The understanding of the physical and catalytic properties of zeolite beta are depend on the knowledge of the structural features of the framework. These properties are mainly affected by crystal size, faulting, and Si/Al mole ratio. Therefore, the effect of the aluminum content on these variables and on the crystallization behavior of zeolite beta was studied by Sagarzazu *et al.* (2005).

### 2.3 Sensors Based on Polymer/Zeolite Composites

Conductive polymers have been widely used in gas sensing applications. In comparison with most of the commercially available sensors, based usually on metal oxides which can operated at high temperatures, the sensors made of conducting polymers have many improved characteristics. The conductive polymer based sensor can be operated at room temperature. They are light, non-corrosive, and can be prepared easily. Due to its advantages, in 2005, the effects of zeolite content, type and ion exchange capacity on electrical conductivity response to carbon monoxide (CO) of polyaniline/zeolite composites were investigated by Densakulprasert *et al.* After this research, the influence of Zeolite A (LTA) on the electrical conductivity response of polyaniline under CO exposure were investigated by the effects of zeolite amount and pore size (Chuapradit *et al.*, 2005).

A conductive polymer, poly(3-thiopheneacetic acid), with a variety of zeolites were fabricated to be used as selective gas sensors. The effects of zeolite type (L, mordenite, and beta), zeolite concentration, cation type, and cation concentration on electrical conductivity sensitivity response of composites were investigated (Thuwachaowsoan *et al.*, 2007). Furthermore polypyrrole (Ppy)/zeolite composite were fabricated by dispersing zeolite particles (molecular sieve 13X) into the Ppy matrix. Electrical conductivity sensitivity and interaction mechanisms between this composites and CO<sub>2</sub>, CO, and SO<sub>2</sub> were investigated. Moreover, the effects of zeolite concentration, cation type, and cation concentration were investigated (Soontornworajit *et al.*, 2007).

Recently, polypyrrole (PPy)/3A zeolite/polyamide 6 composites in the form of electrospun fiber bundle as chemical sensing materials were fabricated in two forms; hydraulic-pressed pellet and solution-cast film. For this work the target

chemical vapors were acetone, methyl ethyl ketone (MEK), methanol, and toluene. Electrical responses and sensitivities of the sensing materials towards these chemical vapors in N<sub>2</sub> had detected (Wannatong *et al.*, 2008).