# CHAPTER II
# LITERATURE REVIEW

Materials in the real world can be categorized into three main classes according to their ability to conduct electricity at room temperature (Chandrasekhar, 2002): (1) *Conductors* such as copper, iron and silver; (2) *Insulators* i.e. quartz, diamond and glass; and (3) *Semiconductors,* materials in this group possess their conductivity between conductors and insulators, e.g. silicon, germanium, and some polymers as called conductive polymers.

## 2.1 Conductive Polymer

Conductive polymer is an organic polymer semiconductor, or organic semiconductor which contains extended π-conjugated systems-single and double bonds alternating along the polymer . The π-conjugation is formed by the continuous overlapping between $p_z$-orbital of the carbon atoms (Figure 2.1), which provides delocalization of these bonds. However, the conjugation is not enough to make the polymer conductive; therefore conductive polymer generally exhibits very low conductivities. The enhancement of conductivity can be achieved by means of a doping process.

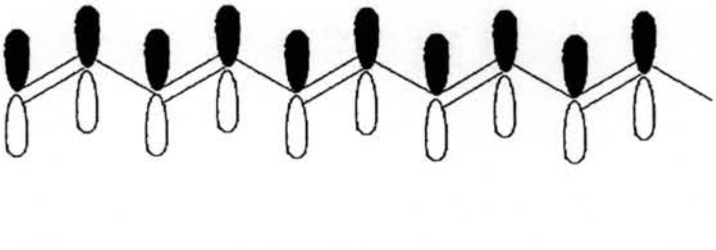

**Figure 2.1** π-conjugation in poly(acetylene).

### 2.1.1 Mechanism of Polymer Conductivity and Doping

The electrical properties of a material are determined by its electronic structure. In a metal, the orbitals of the atoms overlap with the equivalent orbitals of their neighbouring atoms in all directions to form molecular orbitals similar to those of isolated molecules. In a metal, however, any continuous solid-state structure, the number of atomic orbitals is typically about $10^{22}$ for a 1 $cm^3$. When this many orbitals are spaced together in a given range of energies, they form an apparently continuous band of energies as shown in Figure 2.2. The energy spacing between the highest occupied, and the lowest unoccupied, bands are called the *band gap*. The lowest unoccupied band is called the conduction band and the highest occupied band is the valence band.

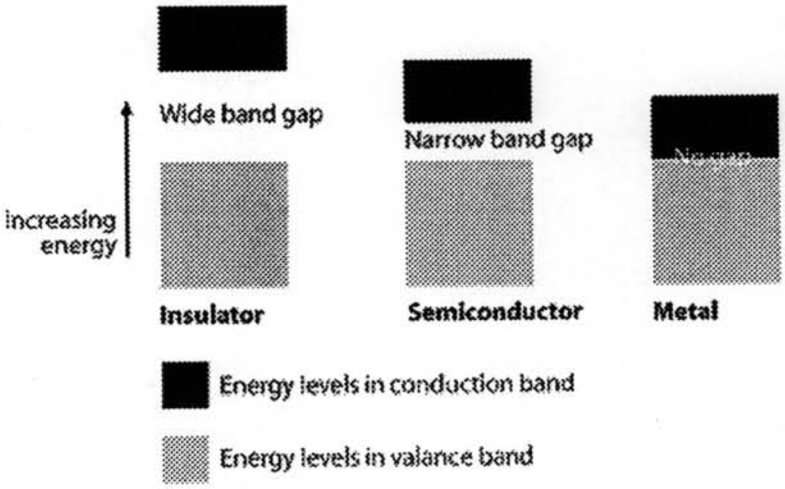

**Figure 2.2** Different band gab of an insulator, a semiconductor and a metal.

The electrical properties of conventional materials depend on how the bands are filled. When the bands are filled or empty, no conduction occurs. If the band gap is narrow, at room temperature thermal excitation of electrons from the valance band to the conduction band gives rise to conductivity which it happens in classical semiconductors. When the band gap is too wide, a thermal excitation at room temperature is insufficient to excite electrons across the gap and become an insulator. The high conductivity of metals is due to partially occupied bands, a partially filled conduction band, a partially empty valance band, or a zero band gap.

The semiconductor band structure of conductive polymer permits electronic excitation or electron removal/addition, e.g. from the valence band to the conduction band, leading to interesting properties of conductive polymers. Excitation of electrons from the balance band to the conductive band can be achieved by a chemical or the oxidation of a conductive polymer: essentially a removal of electrons from the valence band leads to the presence of charges on the polymer chains. These charges are in general strongly delocalized, over several monomer units in the polymer. A charge may also be donated to the conduction band of the polymer, causing a reduction of the conductive polymer. (Chandrasekhar, 2002)

Oxidation caused by a chemical species generates a positively charged conductive polymer and associated anion, which is known as "p-type doping". Reduction similarly generates a negatively charged conductive polymer and associated cation, which is known as "n-type doping". Example of these processes are shown respectively below, in very rough schematics, where M and A are any a cation and an anion, respectively. During the doping, conductive polymer contains both/either polaron and/or bipolaron depending on doping level.

$$\mathrm{PPy + MClO_4 \longrightarrow PPy^+\,ClO_4^-\,M^+} \qquad \text{(Oxidation)}$$

$$\mathrm{PAc + NaA \longrightarrow Na^+\,PAc + A^-} \qquad \text{(Reduction)}$$

Normally, the doping yields the charge concentration directly proportional to concentration of the dopant. Doping of conductive polymers relates the random dispersion or aggregation of dopants in molar concentrations in the disordered structure of entangled polymer chains, leading to the formations of conjugational defects which are solitons, polarons, or bipolarons in the polymer backbone (Kumar and Sharma, 1998).

Common classes of organic conductive polymers include poly(acetylene), poly(pyrrole), poly(thiophene), poly(aniline), poly(fluorene), polynaphthalene, poly(p-phenylene), poly(p-phenylene sulfide), and poly(p-phenylene vinylene), as shown in Figure 2.3.

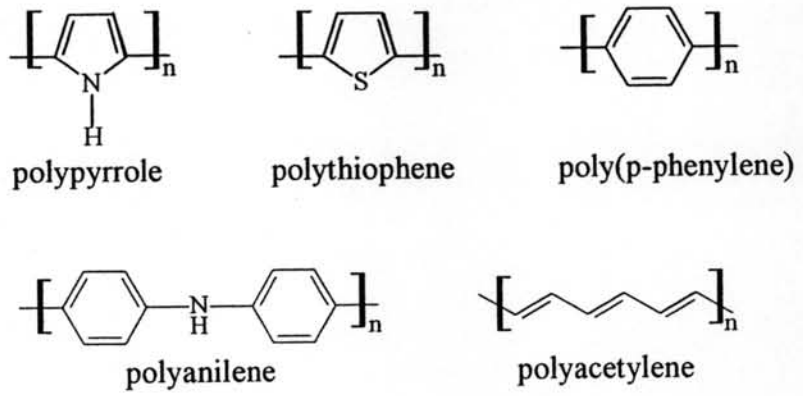

**Figure 2.3** Repeat unit of electrically conductive polymers.

### 2.1.2 Poly(*p*-phenylene)

Poly(*p*-phenylene) (PPP) has been studied as one of electrical conductive polymer which is composed of a linear sequence of phenyl rings; therefore, it possesses outstanding physical and chemical properties. In particular, it is known for its exceptional thermal stability (in the neutral state), its resistance to environmental oxidation and radiation. PPP consists of a rod-like polymer and are therefore insoluble in all organic or mineral solvents (Lacaze *et al.*, 1997).

The synthesis of PPP is related to the general aryl coupling reaction which leads to the C-C bonds between the aromatic nuclei. The different methods used for the chemical synthesis of PPP may be classified into three main reaction families (Lacaze *et al.*, 1997):

(1) Direct oxidation of benzene with a suitable catalyst-oxidant system, usually referred to as the Kovacic reaction
(2) Catalytic and thermal dehydrogenation of poly(1,3-cyclohexadiene)
(3) Metal-catalyzed coupling reaction (Grignard Ullmann, Wurtz-Fitting, Yamamoto and Suzuki)

PPP has in common the fact that it can be doped either with electron-acceptors (*p*-type doping) or electron-donors (*n*-type doping). The case of *p*-doping is carried out with accepter molecules such as $AsF_5$, $SbF_5$, $SO_3$, $FeCl_3$, $SbCl_5$, halogens, etc., while *n*-doping is achieved with alkali metal donors such as Na, K, Li, or carbanions. The initial conductivity of PPP was less than $10^{-10}$ S $cm^{-1}$ and then increase to over $10^4$ $S.cm^{-1}$ when PPP was exposed to $AsF_5$ (Ivory *et al.*, 1979). In the doped state, the PPP bandgap is 3.5 eV. The removal of an electron from the chain leads to the formation of a polaron, whose quinoid-like geometry extends over about five benzenic rings, and leads to two energy levels situated inside the bandgap at about 0.6-0.9 eV from the band edges (Lacaze *et al.*, 1997).When a second electron is removed, a bipolaron is formed, with a geometry more quinoidic than that of the polaron and, therefore, bipolaron level is at a greater distance the band edges than the polaron level (Figure 2.4).

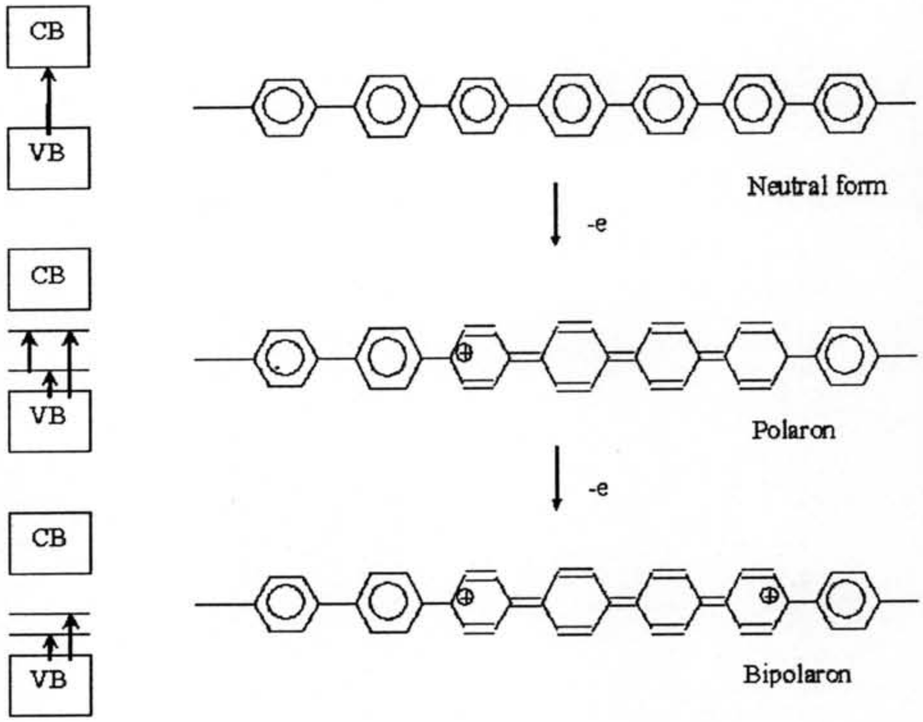

**Figure 2.4** Simplified polaron-bipolaron of PPP.

## 2.2 Zeolites

Zeolites are hydrated, porous, crystalline tectoaluminosilicates, which were discovered in 1756 by the Swedish mineralogist, Cronstedt (Mark and Raul, 1992). They are constructed from a linked $TO_4$ tetrahedral (where T = tetrahedral atom, e.g., Si, Al) jointed through shared oxygen atom between two adjacent tetrahedra (Figure 2.5) giving a framework ratio of O/T = 2. (The term tectoaluminosilicate designates that all the oxygen atoms bridge two tetrahedral atoms.) They have a cage-/channel-like structure of precise geometry of uniform shape through the entire crystal. The cage or channel size can vary approximately between 0.3 and 1.2 nm, allowing these materials to have unexpected properties due to the limited size of the channels. Pure silicate materials ($SiO_2$) do not contain framework charge since silicon is tetravalent. However, aluminosilicates have negatively charged oxide frameworks (one charge per framework $A1^{3+}$) that require balancing extraframework positive ions. Typical cations in natural zeolites are alkali metals, e.g., $Na^+$, $K^+$ and alkaline earth e.g., $Ca^{2+}$, $Ba^{2+}$, ions. In general, zeolites contain cations in their channels; they are partially filled with water molecules in the channels in order to compensate for the internal charge inhomogenities (polar momentums) (Schaf *et al.*, 1997).

Practically, the zeolites are mainly used in catalysis and as sorbents. Due to the limited size of the channels, confinement effects can lead to the formation of unexpected products, resulting in a drastic modification of the selectivities compared to those achieved with more classical supports like silica or alumina. This phenomenon is known as the “shape selectivity”. As the size of the channels is very narrow compared to that of small molecules, the latter can fill them if their kinetic diameter is smaller than the pore entrances. In contrast, larger molecules will not be adsorbed. This effect is usually used for drying liquids, the water molecules being entrapped in the zeolite, or for separation of gases.

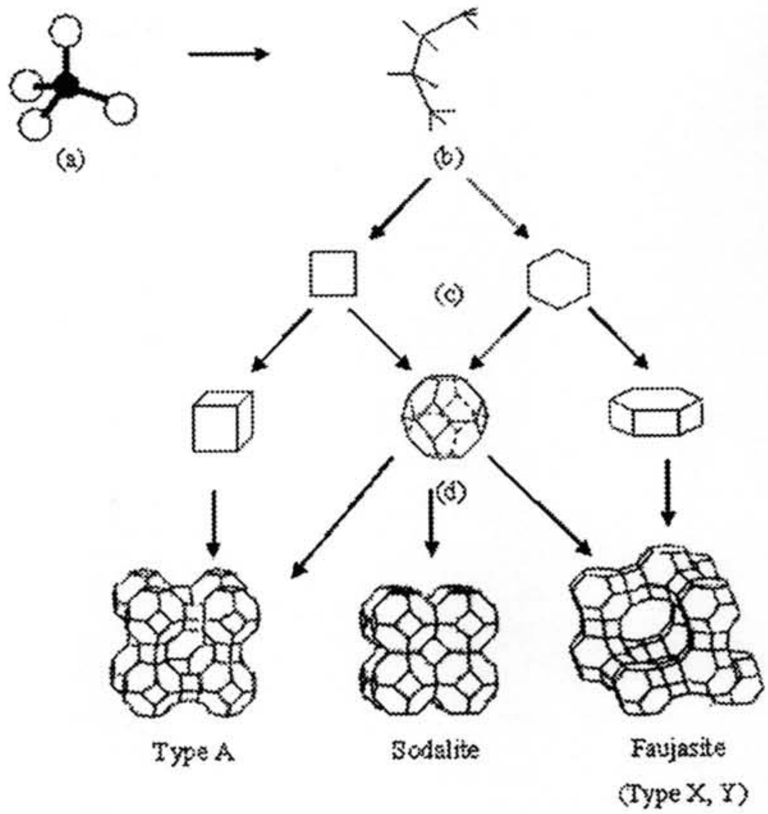

**Figure 2.5** Zeolite constructions: (a) Tetrahedral structure; (b) Tetrahedral structure connected by sharing the oxygen atom; (c) Secondary building units; and (d) Polyhedra forms.

In the zeolite, the interaction between the adsorbed molecule and the framework can mainly be described by Van der Waals strengths. According to the previous word, the framework contains negative changes, due to the presence of aluminium atoms. If the adsorbed molecules are polar (like water or alcohols), supplementary interactions exist between the negative charges of the framework and the adsorbent, resulting in a stronger adsorption. For example, ethanol will be adsorbed more strongly than *n*-hexane, and this adsorption difference between the two molecules allows them to be discriminated by a zeolite with a sufficient amount of aluminium (Hugon *et al.*, 2000).

## 2.3 Poly(*p*-phenylene) Synthesis

Kovacic and Kyriakis (1963) studied poly(*p*-phenylene) synthesis coming from polymerization of benzene under remarkably mild conditions on treatment with aluminum chloride-cupric chloride-water in the ratio of benzene:$AlCl_3$:$CuCl_2$ 2:1:1 by mole with 1 ml of water. The reaction was carried out under nitrogen in a 3-necked flask equipped with a paddle stirrer and allowed to proceed for 30 min at 35-37 °C. The product was in the form of finely divided, light brown solid. Evidence for the synthesized *p*-polyphenyl structure is based upon the C/H atomic ratio which varied from 1.45 to 1.55 with an average of 1.49 being close to *p*-polyphenyl possessing a limiting theoretical C/H atomic ratio of 1.5. The infrared spectrum of prepared polyphenyl gave good evidence for the *para* configuration, with phenyl end groups constituting a minor part of structure. The principal absorption band at 805-807 $cm^{-1}$ and additional bands of secondary intensity were situated at 1000, 1400 and 1480 $cm^{-1}$, these bands are characteristic of the *para* substitution. The reaction is believed to proceed by an oxidative cationic polymerization of the aromatic nuclei.

Kovacic and Oziomek (1964) studied the effects of water, cuprous chloride and variation in catalyst-oxidation ratio on polymer yield. Water was added to the system $C_6H_6$-$AlCl_3$-$CuCl_2$ having the ratio of 4:1:1 (2 hr. at 30-32 °C), in molar ratio of $H_2O$-$AlCl_3$ varying from 0 to 4. The results clearly showed that polymer yield varied inversely with the amount of added water. Additionally, polymer yield attained a maximum value, almost quantitative, at an $AlCl_3$-$CuCl_2$ molar ratio of 2:1. The cuprous chloride formed by reduction of the oxidant was present as a $C_6H_6$-$AlCl_3$-$CuCl$ complex. Large amount of added cuprous chloride inhibited the reaction completely, whereas smaller quantities acted as promoter. Finally, in the presence of aluminum halide catalyst, the polymerization occurred with the various oxidizing agents such cupric chloride, cupric bromide, lead dioxide, manganese dioxide, nitrogen dioxide, nitrogen trioxide, chloranil and, *p*-benzoquinone. The interpretation of infrared spectral data indicated that polymers prepared with nitrogen oxides and chloronil possessed lower molecular weights than the others; therefore, the nitrogen oxides and chloronil revealed themselves as the chain terminators.

## 2.4 Conductive Polymers as Sensors

Conductive polymer is a new class of materials possessing the highly reversible reduction/oxidation behaviour along with the combination of properties between metal and plastics. Therefore, the conductive polymer is a possible substitution for metals and semiconductors in the electrical and electronic industries and even in the optoelectronic industrial field. The potential applications of conductive polymer involve in many growing technologies such as rechargeable batteries, capacitors, electrooptical display devices, and sensors (Kumar and Sharma, 1998).

The application of conductive polymer as sensors is one of the current trends. Conductive polymer can be prepares for several different intentions and offer a unique interface interaction between the sensors and target molecular receptors. Thus, there are several conductive polymers used as the sensors: e pH sensors (Kaden *et al.*, 2004); ion-selective sensors (Migdilski *et al.*, 1996); humidity sensors, (Nohria *et al.*, 2006); biosensors (Grennan *et al.*, 2006); and gas sensors (Persaud, 2005).

Gas sensors have been of interest for the safety reason and for the control of the amounts of the gases in various industrial processes. Brady *et al.* (2005) investigated the chemical sensing capabilities of a smart textile based on PPy coated on the PU foam substrate. This smart fabric offered a higher selectivity toward ammonia over other volatile organic vapors such as hexylamine, acetone propanol and water.

Jang and Bae (2006) fabricated PPy-coated carbon nanofiber (CNFs) for irritant gas detection. $NH_3$ and HCl caused the decrease and increase in the electrical conductivity due to the dedoping and the oxidizing of the conductive layer, respectively. The sensors exhibited an enhanced response signal due to the presences of the thinness, uniformity, and more active sites of PPy layers on the CNF surface. The responses of the sensors after interaction with $NH_3$ and HCl were reversible and reproducible and dependent on the thickness of the PPy layers.

Rosa *et al.* (2005) prepared poly(2-bromo-5-hexyloxy-p phenylenevinylene), BHPPV. Synthesized gas sensors were made from thin films of 10-camphorsulfonic acid doped BHPPV, deposited on interdigitated electrodes. They responded to five different solvents: acetone, hexane, water, methanol and ethanol. The sensors exhibited quite different responses to the tested vapours. In cases of acetone and hexane, the resistance increased, while for the other solvents it decreased. Plots of relative response versus relative recovery showed good discrimination of the five solvents.

Watcharaphalakorn *et al.* (2005) blended PANI with polyimide (PI) to improve mechanical, thermal behaviours of the conductive polymer. The addition of PI also enhanced the sensitivity response of the blends towards CO gas. The target gas such CO acted as an electron withdrawer and the interaction of gas and polymer phase was proposed to occur at the –NH– attack site which contained the lone pair of electron; the proposed interaction caused the increase in the conductivity of doped PANI due to the increase of the number of charge carriers on the polymer chain.

Reemts *et al.* (2004) prepared and characterized conductive layers of emeraldine base polyaniline (PANI) and tested them as a transducer for gas/organic vapor sensors. Ethanol and acetone were chosen as model compounds to be studied on the PANI films while ammonia performs as reference, the sensitivity of the films against these gases was investigated. In test reactions with volatile organic vapors or with $NH_3$, it was shown that changes in the doping level of PANI provided a significantly more sensitive signal. The films tested provided a good sensitivity against $NH_3$ with a linear dependence of the signal on concentration in the parts per million ranges.

Hong *et al.* (2004) prepared an ammonia gas sensor by polymerizing aniline on the surface of nylon 6 fabrics and doped with various acids. The fabricated polyaniline (PANI)–nylon 6 composite fabrics showed high sensitivity and fast response for $NH_3$ gas compared to those of CO and $C_3H_8$. The electrical resistance of the PANI–nylon 6 composite fabrics increased when exposed to an ammonia environment but reversibly recovered after flushing with fresh air. In particular, the PANI–nylon 6 composite fabrics doped by monocarboxylic acids (such as formic acid, acrylic acid, and trichloroacetic acid) displayed excellent sensitivity and fast response. Moreover, no significant changes in the $T_m$ and crystallinity were found in these composite fabrics. Hence the PANI–nylon 6 composite fabrics were attractive alternatives for use in sensing applications because of their excellent sensing ability, low cost, and ease of preparation.

Jain *et al.* (2003) reported the behaviour of humidity sensors with polyaniline-based conducting polymers doped with different weak acidic dopants. Changes in surface resistivity of films were monitored as a function of relative humidity. The acidic dopants used were camphosulphonic acid (CSA), diphenyl phosphate (DPPH), and maleic acid (Mac) blends of these were formed with styrene–butyl acrylate copolymer for improving the mechanical stability. The sensitivity of responding the level of relative humidity was compared for three composites wherein, although low sensitivity the Mac-doped films were found to be repeatable and more stable compared to the others. Films prepared form styrene–butyl acrylate copolymers with different concentrations of PANI–Mac were used for sensing humidity ranging between 20 and 95% relative humidity. The films exhibited almost linear behaviour within a chosen range of humidity.

Bhat *et al.* (2003) prepared polypyrrole–poly(methylmethacrylate) (PMMA+PPy) blend films. The mechanical properties of the conducting PMMA+PPy films were studied and found to be improved relative to the PPy films. The electrical conductivity of the PMMA+PPy film was measured by using a standard four- and two-probe. The conductivity of the films depended on the pyrrole content. These conducting composites were further used as gas sensors by observing the change in the current when exposed to ammonia gas. The film gave a fast and reproducible response towards ammonia gas.

Gangopadhyay and De (2001) prepared a polypyrrole (PPy)-based conducting composite within crosslinked matrix of poly(vinyl alcohol) (PVA). The blend was found to possess significant $NH_3$ sensing capacity. $NH_3$ being an electron donating gas, resulted in an enhancement of the resistance of the PPy film. With increasing $NH_3$ concentration, more obvious changes were observed but an $NH_3$ concentration above 10% resulted in almost irreversible change in resistance; the mechanism of $NH_3$ sensing response was not indentified.

Lin *et al.* (1998) prepared methanol sensors based on PPy-PVA composite films. The sensing abilities, including sensitivity, response time and recovery time, to various methanol-vapor concentrations were investigated. The incorporation of an appropriate amount of PVA (about 7.5 $g\ l^{-1}$) improved the sensitivity of PPy-based sensors to methanol vapor up to nine times. The composite sensor had a quicker response in a relatively higher methanol concentration. However, the incorporation of PVA in the composite sensor lowered both the response and the recovery speed as compared to those of the pure PPy sensor. The incorporation of PVA also reduced the stability of the sensor when it was exposed to a methanol environment, probably owing to the hydrophilic nature.

Collins and Buckley (1995) presented a novel sensing format for the detection of toxic vapors. They used thin films of conductive polymers, polypyrrole or polyaniline, coated onto poly(ethylene terephthalate) or nylon threads woven into a fabric mesh. Chemical sensing on fabrics offered the opportunity of using the large surface area for improved sensitivity and expanded dynamic range. The resistivity of these materials was monitored following exposures to several toxic gases. The results showed that low ppm detection limits have been demonstrated for toxic gases such as ammonia and nitrogen dioxide, as well as the chemical warfare stimulant, dimethyl methylphosphonate (DMMP). Polymeric overcoats including polyethylenimine and fluoropolyol were evaluated as a means of introducing selectivity and sensitivity with respect to the adsorption of particular classes of gas analytes.

## 2.5 Zeolites as Gas Adsorbents

Schaf *et al.* (2006) investigated the shape-selective resistivity of gas sensors for polar molecules by using the stilbite zeolite. The interaction between zeolite and incoming molecules can be described by the Langmuir-type adsorption. The conductivity changes when the sensors were exposed to the gas was interpreted mainly by the difficulty of exchangeable cation mobility, due to sterical interactions in the zeolite channels, the size and the dipole moment of the molecule.

Vilaseca *et al.* (2006) developed and tested a new type of sensor, namely a quartz crystal microbalance (QCM) modified by a layer of $AlPO_4$-18 crystals in gas sensing applications. The performance of the sensor was compared to that of other QCM devices modified by different zeolite materials (zeolite A and silicalite). The $AlPO_4$-18 modified sensors were sensitive to water and other polar molecules of small size. On the other hand, their affinity towards non-polar molecules was low, thus enabling the sensing of water in the presence of hydrocarbons.

Sahner *et al.* (2006) modified electrodes by using ZSM-5 zeolite as a cover layer of the electrodes in order to enhance response ability to hydrocarbons. The ZSM-5 cover layer caused the sensor better to detect propane or butane than films without the ZSM-5 layer.

Huang *et al.* (2004) modified QCM with $Ag^+$-ZSM-5 zeolite to diagnose diabetes. Such sensor was utilized in detecting acetone in nitrogen and the concentration of acetone in diabetics' breath. The experimental results demonstrated that the QCM coated with $Ag^+$-ZSM-5 zeolite had a high sensitivity and selectivity with good repeatability. A test for minimum detectable concentration of acetone vapor went as low as 1.2 ppm, and the lower detection limit of acetone vapor was conceived to be much lower. 0.26 ppm was identified in the diagnosis of diabetes. The breath between diabetics and healthy persons were well distinguished. An average of 90s response time was observed. The frequency shift of QCM along with temperature was studied as well.

Rauch and Liu (2003) reported that the utilization of zeolite A film coated on the sensors can selectively limit gas exposure. The sensor without a zeolite layer exhibited a strong response to both oxygen and carbondioxide in the mixture of these gases. With the zeolite film coated, the sensor was able to discriminate the responses between the two gases. The modified sensor only showed the response to oxygen, leading to the conclusion that oxygen diffusion through the zeolite was preferential to $CO_2$ diffusion. Therefore, it can be concluded that the sensor response of different gases depending upon the diffusion ability of gas through the zeolite and the sensing surface.

Zhou *et al.* (2003) developed a novel freon gas sensor of piezoelectric microcantilever coated with zeolite in order to control indoor air quality. The microcantilever was employed to detect the concentration of sample freon-12 gas ranging from 0 to 100 ppm by the effect of the specific MFI zeolite modification. High selectivity and sensitivity combined with excellent repeatable and reversible performances were shown. The minimum mass changing of $3.5 \times 10^{-9}$ g and the sensitivity of $-0.0024\%$/ppm were determined from the experiments.

Vilaseca *et al.* (2003) developed semiconductor (Pd-doped $SnO_2$) gas sensors covered with zeolitic films (MFI or LTA) for being used as a gas phase sensing of different species (methane, propane, and ethanol) at different humidity levels. The dynamic responses obtained with these sensors were compared with the response of a reference sensor without a zeolitic layer. The results clearly indicated that a suitable zeolite layer strongly reduced, and in some cases suppressed, the response of the sensor to paraffins, thereby increasing the sensor selectivity to the alcohol, while the reference sensor could not discriminate between these molecules. This clearly showed the potential of zeolite-based sensors to achieve a higher selectivity/sensitivity in gas sensing applications.

Hugon *et al.* (2000) used a molecular filter exposed at the heads of sensors which had poor selectivity towards many chemicals in order to enhance this property. It was shown that such filter with zeolite was tested with a semiconductor and optical chemical sensors.

Li and Kawi (1999) prepared the MCM-41 modified $SnO_2$ for gas sensing application by mechanically mixing $SnO_2$ with MCM-41. $H_2$, CO and $CH_4$ were used to investigate the sensing properties of the sensors. The sensor modified by MCM-41 gave the higher sensitivities and selectivity to $H_2$, CO and $CH_4$ than the unmodified one. However, in cases of CO and $CH_4$, the sensitivities of modified sensors were improved at much higher temperature range. They also briefly discussed the mechanistic aspect that the pore structures and the adsorption properties of MCM-41 may be assignable for the improvement of sensing properties of SnO2 modified by MCM-41.

Fukui and Nishida (1997) found that Ferrierite, one of siliceous zeolite, had a prominent ethanol filtering effect. It was found that coating on the CO selective gas-sensor based on $La_2O_3Au/SnO_2$ ceramics, a high selectivity towards CO was obtained amongst $H_2$, $CH_4$, i-$C_4H_{10}$ and $C_2H_4$. Ferrierite exhibited an acidic catalyst layer converting $C_2H_5OH$ into $C_2H_4$ with a low sensitivity by dehydration. The prominent performance was related to a strong acid strength and a large acid amount. Additionally, the siliceous zeolites have a hydrophobic property, a specific area and a thermal stability. As a result, a CO selective gas sensor with sensitivity to CO over ten times higher than that to the other gases

## 2.6 Conductive Polymer/Zeolite Composite as Sensors

Soontornworajit *et al.* (2007) investigated the electrical conductivity sensitivity and interaction mechanisms between mechanically mixed polypyrrole(PPy)/13X composites and $CO_2$, CO, and $SO_2$. There were negligible negative responses of PPy when exposed to $CO_2$, and CO in contrast to definite positive responses towards $SO_2$ in which the interaction was irreversible. Undoped PPy and doped PPy composites containing 10% (v/v) of 13X had the highest sensitivity to $SO_2$. Adding fully $Na^+$ exchanged zeolite into PPy matrix provided the highest electrical conductivity sensitivity toward $SO_2$.The sensitivity of Ppy/13X composite to $SO_2$ diminished as the cation $Na^+$ was exchanged to other alkali cations in this decreasing order: $Cs^+$, $K^+$, and $Li^+$, in the opposite order to the binding energy between the gas and the cations. The sensitivity and interaction were also reduced with increasing amount of $Li^+$ present.

Densakulprasert *et al.* (2005) studied the effects of zeolite content, pore size and ion exchange capacity on electrical conductivity response to CO of PANI/zeolite composites. Zeolite Y, 13X, and synthesized AlMCM41, all having the common cation $Cu^{2+}$, were dry mixed with synthesized maleic acid doped PANI and compressed to form PANI/zeolite pellet composites. The addition of 13X zeolite to pristine PANI, the electrical conductivity sensitivity to $CO/N_2$ gas increased with zeolite content. For the effect of zeolite type, the highest electrical conductivity sensitivity was obtained with the 13X zeolite, followed by Y zeolite, and AlMCM41, respectively. Poor sensitivity of AlMCM41 was probably due to its very large pore size and its lowest $Cu^{2+}$ exchange capacity. Y zeolite and 13X zeolite have comparable pore sizes but the latter has a greater pore free volume and a more favorable location distribution of the $Cu^{2+}$ ions within the pore. The temporal response time increased with the amount of zeolite in the composites but it was inversely related to the amount of ion exchange capacity.

Chuapradit *et al.* (2005) utilized LTA zeolites mixing with PANI for acting as CO sensor. The improvement of electrical sensitivity of PANI towards CO was accomplished by adding zeolite 4A up to 40% w/w. Zeolite 5A was the most effective mesoporous material in promoting interaction between CO and polyaniline because of its largest pore size of 5 A°, relative to the zeolite 3A and 4A which have the pore sizes of 4 and 3 A°, respectively. The reversible interaction between CO and PANI occurred at amine nitrogen or at the polaron species.

Enzel and Bein (1998) designed a model system via an encapsulation of polymeric chain conductor in low-dimentional, ordered lattice of a zeolite in order to reduce the size of electronic circuitry to molecular dimension. Polyaniline was synthesized in the channel of mordinite (one-dimension) and zeolite Y (three-dimension). The results showed that the polyaniline chains in mordenite channels appeared to be more highly oxidized than in zeolite Y. The conductivity of polymer/zeolite sample ($< 10^{-8}$ S/cm) was lower than the bulk conductivity of undoped polyaniline ($\approx 10^{-6}$ S/cm). The level of intrazeolite reaction or the nature of the channel system controlled the degree of polymer oxidation.

Wu and Bein (1994) prepared a conducting polymer, polyanilne, in a three-nanometer wide hexagonal channel system of MCM-41. The oxidative polymerization occurred by an adsorption of aniline vapor into the dehydrate host. Spectroscopic data showed that the filaments were in the protonated emeradine salt form, and chromatography indicated chain lengths about 190 aniline rings. The significant low-field conductivity of the polymer filaments as measured by microwave absorption at 26 GHz demonstrated that the conjugated polymer could be encapsulated in nanometer channels and still supported mobile charge carrier. This demonstration represented a step toward the design of nanometer electronic devices.

## 2.7 Poly(*p*-phenylene) as a Gas Sensor

Blackwood and Josowicz (1991) studied the interaction between conductive polymers (PPP and PPy) and organic vapors by employing UV/visible method which followed the charges in the polaron and bipolaron concentrations, and sensed any charge transfer of the conductive polymer films. The methanol exposure caused a reduction of poralon and/or biporalon concentration in the polymer films due to the methanol acting as an electron donor. The steps of the interaction were proposed, which consisted of: the interaction of the vapor molecules toward the polymer, the partial charge transfer to/form a mid-gab state in the film, and the lateral dispersion of the charge between all the adsorbed molecules.

Yamamoto and Gu (1986) studied the effect of ammonia gas on electrical property of conducting polymer. The conductivity of the PPP film was increased by several orders of magnitude when exposed to $NH_3$. The change in electrical conductivity took place relatively fast and was reversible. When the partial pressure of $NH_3$ was reduced by evacuating the sample chamber the electrical conductivity of the PPP film decreased in a similar but reversed way to that. From these results, it could be concluded that $NH_3$ acted as an effective doping agent in n-doping of PPP. Similar results were obtained when PPP films were exposed to diethylamine and triethylamine. There was a suggestion that PPP can be used as a new type of sensor for $NH_3$ gas and odors with a very simple structure.