

CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1 Theoretical Background

2.1.1 Gas Sensors

Recently, the most common problems in many countries of the world are rigorous environmental standards and regulation on hazardous and flammable gas. These include hydrocarbons, oxygen, and other various gases chemicals. Thus, they need to be monitored to protect against the unwanted incidence of fire or explosion (Aswal and Gupta, 2007). Table 2.1 shows Threshold Limit Value (TLV) data of the common toxic gases. It has seen that most of these gases must be detected at parts per million (ppm) levels in the ambient. While other gases (for example H₂) are not toxic at ppm levels but they are combustible and form explosive mixtures when their concentration in air exceeds a threshold value. Table 2.2.

Table 2.1 Long and short term exposure limits of some typical toxic gases/vapors

Gas/Vapor	Long-Term Exposure Limit, 8 hr (ppm)	Short-Term Exposure Limit, 10 min (ppm)
H₂S	10	15
CO	50	300
NO_x	3	5
SO₂	2	5
PH₃	-	0.3
CH₃OH	200	250
Cl₂	0.5	1
NH₃	2.5	35
HCl	-	5

Table 2.2 Lower explosive limit and ignition temperature of some typical combustible gases/vapors

Gas/Vapor	Lower Explosive Limit (%v/v)	Ignition Temp. (°C)
H₂	4	560
CO	12.5	605
CH₄	5	595
CS₂	1	102
C₄H₁₀	1.5	365
CH₃OH	6.7	455
Kerosene	0.7	210
C₂H₆	3	515
C₂H₂	1.5	305

In order to monitor different gases, varieties of gas sensing materials have been developed and, many of them are available commercially. In principle, a gas sensor converts the gas concentration into a physical signal such as current, absorbance, mass or acoustic variables. Table 2.3 gives a summary in advantages, disadvantages, and application fields for sensing materials.

Table 2.3 Summary of basic gas sensing materials (Liu *et al.*, 2012)

Material	Advantages	Disadvantages	Application Field
Metal Oxide Semiconductor	<ul style="list-style-type: none"> a) Low cost: b) Short response time; c) Wide range of target gases: d) Log lifetime 	<ul style="list-style-type: none"> a) Relatively low sensitivity and selectivity: b) Sensitive to environmental factor c) High energy consumption 	<ul style="list-style-type: none"> a) Industrial applications and civil use
Conductive Polymer	<ul style="list-style-type: none"> a) High sensitivity; b) Short response time; c) Low cost of fabrication; d) Simple & portable structure; e) Low energy consumption 	<ul style="list-style-type: none"> a) Long time instability; b) Irreversibility; c) Poor selectivity 	<ul style="list-style-type: none"> a) Indoor air monitoring; b) Storage place of synthetic products as paints, wax of fuels; c) Workplaces like chemical industries
Carbon Nanotube	<ul style="list-style-type: none"> a) Ultra-sensitive; b) Great adsorptive capacity; c) Large surface-area-to-volume ratio; d) Quick response time; e) Low weight 	<ul style="list-style-type: none"> a) Difficulties in fabrication and repeatability; b) High cost 	<ul style="list-style-type: none"> a) Detection of partial discharge(PD)
Moisture Absorbing Material	<ul style="list-style-type: none"> a) Low cost: b) Low weight; c) High selectivity to water vapor 	<ul style="list-style-type: none"> a) Vulnerable to friction and repeatability; b) High cost 	<ul style="list-style-type: none"> a) Humidity monitoring

2.1.2 Sensors based on Conductive Polymers

Many different types of gas sensors have been employed for the analysis of volatile organic compounds (VOCs). Perhaps the most competitive type is based on the change in electrical DC resistance (or AC impedance) when a semi-conductive material is exposed to a vapor (Li *et al.*, 2008). These sensors are often made from metal oxide semiconductors or conductive polymers (James *et al.*, 2005). Conductive polymers-based sensors demonstrate a number of attractive features including reversible operation at ambient temperature, high sensitivity to a wide range of VOCs, large possibilities of structural variations, and relative low cost (Li *et al.*, 2008). The most commonly applied conductive polymers for gas-sensing purposes have been polypyrrole (PPy), polyaniline(PANI), and polythiophene (PTh) (Melo *et al.*, 2005; Anitha *et al.*, 2003; Carvalho *et al.*, 2007; Chang *et al.*, 2006). Table 2.4 shows different polymers that used in gas sensors based on different working principles.

Table 2.4 Polymers used as various gas sensors

Gas	Principles	Polymer	Sensor characteristics	Ref.
NH ₃	Change in optical-transmittance using a 2 nm laser (He-Ne) source	PANI-PMMA	Sensitivity of PANI-PMMA coatings are ,10-4000 ppm, reversible response	Nicho <i>et al.</i> , 2001
	Electrical property measurement	PPy	Response time <20 s, recovery time ~60 s	Yadong <i>et al.</i> , 2000
	Electronic property of the film played the part in NH ₃ sensing	PPy-PVA Composite	Resistance increases with NH ₃ concentration but becomes irreversible beyond 10% NH ₃	Gangopadhyay <i>et al.</i> , 2001
NO ₂	Electrical property measurement	PANI- isopolymolybdic acid nanocomposite	Resistance increases with NO ₂ concentration	Li <i>et al.</i> , 2000
	Amperometric gas sensor	SPE (10% PVC, 3% tetra butyl ammonium hexafluoro-phosphate, 87% 2-nitorphenyl octyl ether)	Sensitivity is 277 nA/ppm, recovery time is 19 s	Hlo and Hung, 2000

Table 2.4 Polymers used as various gas sensors (Cont.)

Gas	Principles	Polymer	Sensor characteristics	Ref.
NO	Amperometric gas sensor	Polydimethylsiloxane (PDMS)	Shows sensitivity to 20 nM gas, high performance characteristics in terms of response time and selectivity	Mizutani <i>et al.</i> , 2001
O₂	Amperometric gas transducer	Polydimethylsiloxane (PDMS)	Analyte can be measured up to 1.2 mM	Mizutani <i>et al.</i> , 2001
SO₂	QCM-type gas sensor	Amino-functional poly (styrene-cochloromethyl styrene) derivatives	DPEDA functional copolymer with 5 wt% of siloxane oligomer shows 11 min response time and good reversibility even near room temperature (50 °C)	Matsuguchi <i>et al.</i> , 2001

2.1.3 Conductive Polymers

Polymers have long been considered as insulating materials which are used to coat electric wires to protect them from short circuits. In 1958, polyacetylene (PA) was first synthesized by Natta *et al.* as black powder. This was found to be a semi-conductor with conductivity between $7 \cdot 10^{-11}$ to $7 \cdot 10^{-3}$ S/m. In 1970, Shirakawa *et al.* prepared a silver film from PA and used a Ziegler-Natta as catalyst (K. Ziegler and G. Natta, 1974). In spite of its metallic appearance, it was not a conductor. However, Shirakawa *et al.* (1977) discovered that the oxidation with chlorine, bromine or iodine vapor made PA films 10^9 times more conductive than they were originally states. The treatment with halogen is called doping. The doped form of PA had a conductivity of 10^5 S/m (Shirakawa *et al.*, 1977).

Conductive polymers have conjugated double bonds along the backbone. Every bond contains a strong sigma (σ) bond and a weaker pi (π) bond, so the conjugation can occur along the polymer backbone. Hence conductive polymers have the electrical conductivity property. However, the conductivity of pure conductive polymers is rather low, thus doping process is necessary to achieve highly conductivity.

Other polymers have extensively studied since early 1980s including polypyrrole (PPy), polythiophene (PTh), polyphenylene vinylene (PPV) and polyaniline (PANI). Since PA is very sensitivity to O_2 in air and humidity, PPy and PTh differ from polyacetylene as they it can be synthesized directly in the doped form and very stable in air (Kumar and Sharma, 1998). Conductive polymers are widely used in many applications because of their advantages: light weight, less expensive, high sensitive and short response time at room temperature, easy to synthesis, and their molecular chain structure can be modified conveniently by copolymerization and structure derivations (Bai *et al.*, 2007).

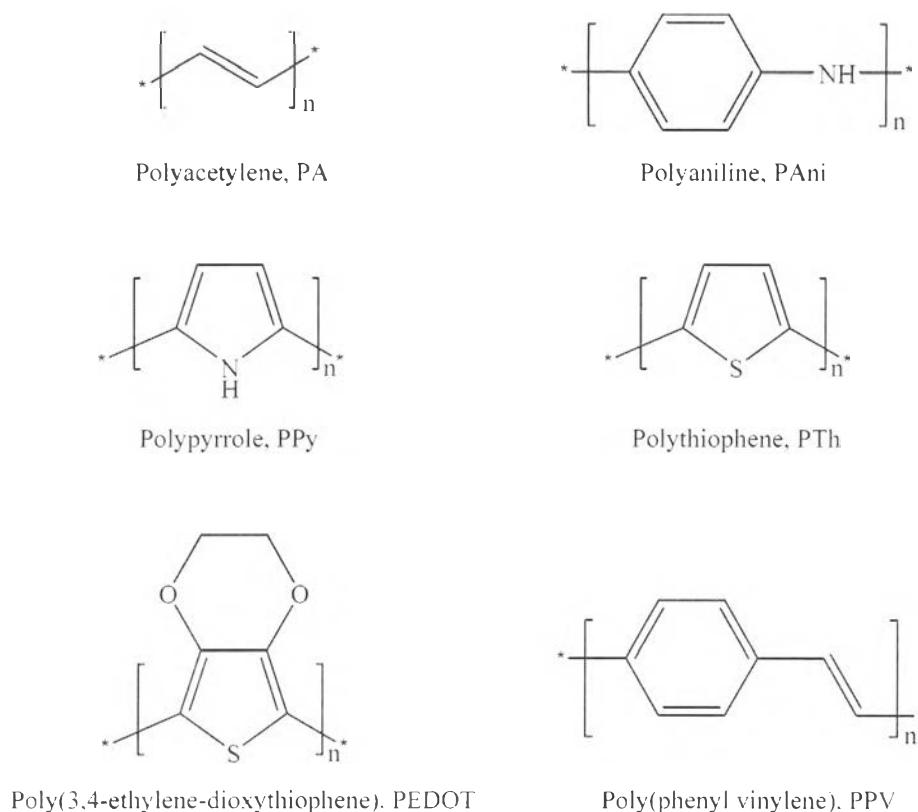


Figure 2.1 The chemical structure of conductive polymers (Bai *et al.*, 2007).

2.1.4 Nanostructure of Conductive Polymers

Nanoscience and nanotechnology are of interest among many investigators because the properties of nanomaterials and bulk materials are quite different. Nanomaterials have large effective surface area, low density, and distinct optical, physical, chemical, electronic and magnetic properties (Jing, 2010; Wang *et al.*, 2008). Control over the size and shape of the nanomaterials plays an important role in tuning their unique properties. Various synthesis strategies, such as hard/soft template (Jing, 2010; Wang *et al.*, 2008; Pang *et al.*, 2005; Vito and Martin, 1998), rapid mixing (Huang and Kaner, 2003), emulsion (Anilkumar and Jayakanan, 2007), chemical, electrochemical (Massoumi *et al.*, 2010), mechanochemical (Palaniappan and Manisankar, 2011), and interfacial polymerization (Huang *et al.*, 2002; Sawall *et al.*, 2004) have been widely employed to control the shape and size. These approaches are of growing interest in the conductive polymer field (Jing, 2010) because conductive polymers on a nano scale are known to exhibit several advantages over

micro scale polymers for various applications: sensors, actuators, electrochromic materials, drug delivery systems (Wan, 2008; Arici *et al.*, 2003; Jang, 2006; Yoon and Jang, 2009). Nanostructure conductive polymers have been synthesized and reported: polyaniline (King and Roussel, 2009; Srinivas *et al.*, 2012; Wang *et al.*, 2006), polypyrrole (Wang *et al.*, 2006; Tungkavet *et al.*, 2012), polythiophene (Gok *et al.*, 2007) and poly(3,4-ethylenedioxythiophene) (Jing, 2010; Paradee and Sirivat, 2013).

2.1.5 Doping Process

Conductive polymers have conjugated double bonds along the backbone. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized sigma (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a weak localized pi (π) bond. However, conjugation is not enough to make the polymer material conductive. In order to increase the conductivity of the conductive polymer, doping process is necessary (Shirakawa *et al.*, 1977).

Doping of conductive polymers can be done either chemically or electrochemically. In the chemical doping the oxidation is accomplished by exposing the conductive polymers to oxidizing vapors. The primary methods of doping conductive polymers are the n-doping and the p-doping. For the n-doping process, the dopant is an electron donor and it injects an electron into a polymer, the extra electron jumps to the neighboring bond. Hence a charge carrier occurs on the polymer backbone, leading to conductivity of conductive polymer. For the p-doping process, the dopant, which is an electron acceptor, creates a hole on the polymer backbone, so the electron from neighboring bond jumps in to fill the hole. Thus conductivity of conductive polymer occurs (Shirakawa *et al.*, 1977).

The first step of doping mechanism is the formation of cation or anion radical, which is called polaron or soliton. Next step is a second electron transfer to form a dication or dianion known as bipolaron. After the first redox reaction, charge transfer complexes may form between charged and neutral segments of the polymer when possible.

(http://www.ch.ntu.edu.tw/~sfcheng/HTML/material95/Conducting_polymer.pdf).

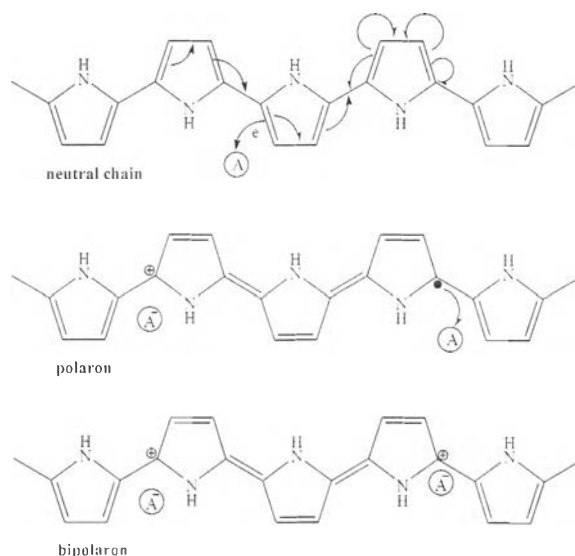


Figure 2.2 Example of doping mechanism of polythiophene

(http://www.ch.ntu.edu.tw/~sfcheng/HTML/material95/Conducting_polymer.pdf).

2.1.6 Polydiphenylamine

Diphenylamine (DPA), an N-substituted aniline derivative, was synthesized to polydiphenylamine (PDPA) by the electrochemical or the oxidative polymerization. This mechanism occurs via a 4, 4' C-C phenyl-phenyl coupling mechanism. The structure of PDPA is intermediate between polyaniline and poly(p-phenylene) (Hua *et al.*, 2003). PDPA can be synthesized directly in the doped form or easily doped with HCl solution to obtain polaron or bipolaron form. PDPA shows many properties that are not comparable with another polymer of N-substituted aniline derivative, these include electrochemistry, conductivity, and electrochromism (Dao *et al.*, 1989; Guay *et al.*, 1990). Furthermore, several investigators have tried to synthesize nanostructure polydiphenylamine (nPDPA) by several techniques such as electrochemical (Zhao *et al.*, 2005; Santhosh *et al.*, 2009), chemical oxidative (Massoumi *et al.*, 2010), and mechanochemical polymerization (Palaniappan and Manisankar, 2011).

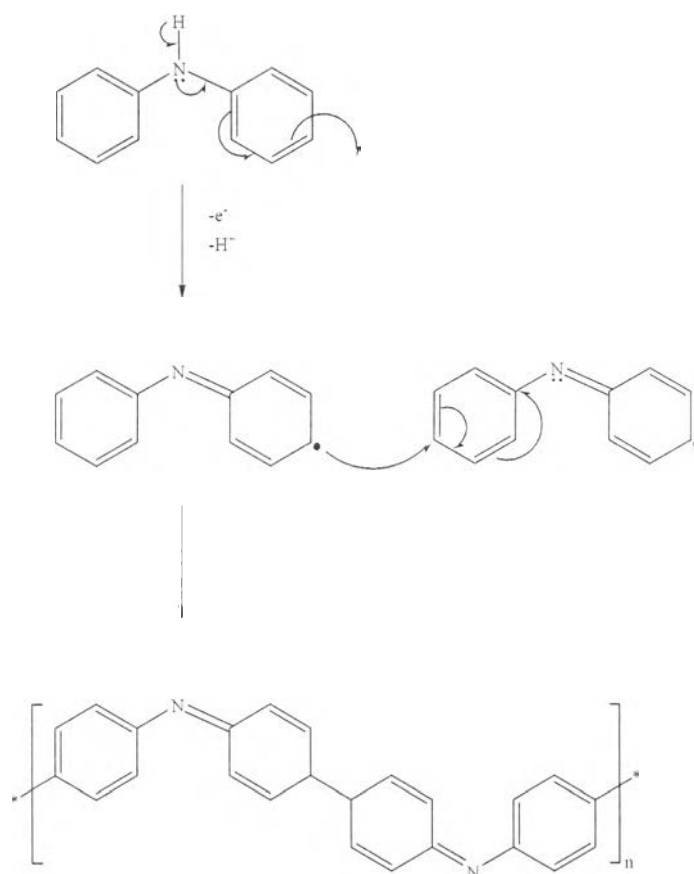


Figure 2.3 Coupling mechanism of polydiphenylamine.

2.1.7 Interactions between Gas Molecules and Conductive Polymers

The interactions between the analytes and sensing materials are multiform, according to different analytes and different active materials which are strong and weak interaction between analytes and conductive polymers.

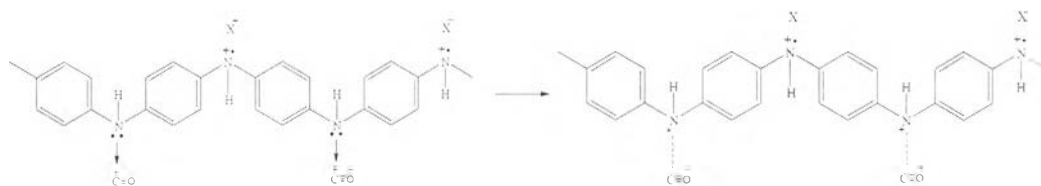


Figure 2.4 Example of interaction between gas molecules and conductive polymers.

2.1.8 Chemical Reactions between Analytes and Conductive Polymers

The physical properties of conductive polymers strongly depend on their doping levels. The doping level of conductive polymers can be easily changed by chemical reactions with many analytes at room temperature and this provides a simple technique to detect the analytes. Most of the conductive polymers are doped/undoped by redox reactions; therefore, their doping levels can be altered by transferring electrons from or to the analytes. Electron transferring can cause the changes in resistance and work function of the sensing material. The work function of a conductive polymer is defined as the minimal energy needed to remove an electron from bulk to vacuum energy level. This process occurs when PPy, PTh and in some case PANI films are exposed in NH_3 , NO_2 , I_2 , H_2S and other redox-active gases (Nguyen *et al.*, 1999; Van *et al.*, 2001; Xie *et al.*, 2002; Mello *et al.*, 2002; Bhat *et al.*, 2003; An *et al.*, 2004; Li *et al.*, 2004; Elizalde *et al.*, 2004; Ram *et al.*, 2005). Electron acceptors, such as NO_2 and I_2 , can remove electrons from the aromatic rings of conducting polymers. When this occurs at a p-type conductive polymer, the doping level as well as the electric conductance of the conductive polymer is enhanced. An opposite process will occur when exposed to an electro-donating gas.

2.1.9 Weak Interactions between Analytes and Conductive Polymers

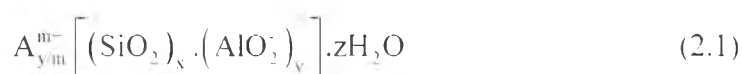
Many important organic analytes, such as benzene, toluene and some other volatile organic compounds (VOCs) are not reactive at room temperature and under mild conditions. Therefore, it is difficult to detect them by their chemical reactions with conductive polymers. However, they may have weak physical interactions with the sensing polymers, involving absorbing or swelling the polymer. These interactions do not change the oxidation levels of conducting polymers, but can also influence the properties of the sensing materials and make these gases detectable.

2.1.10 Zeolite

Zeolites are a family of inorganic, crystalline materials. They consist of interconnected aluminosilicate building blocks, i.e., AlO_4 or SiO_4 tetrahedra, which form 3-dimensional (3D) frameworks with linked channel systems and well-defined micro- and mesopores. At the same time, this high degree of open porosity gives rise

to an exceptionally high-surface area. The database of the International Zeolite Association (IZA) comprises structural information and crystallographic data of more than 170 framework types. At present, only about 17 of these structures are of commercial interest (Maesen *et al.*, 2007).

In addition to the 3D framework of one particular zeolite, the chemical composition is importance in defining its specific properties. Generally, the following sum formula applies (Weitkamp, 2000):



where A is cation with the charge m, (x+y) is the number of tetrahedral per crystallographic unit cell and x/y is the framework silicon/aluminum ratio.

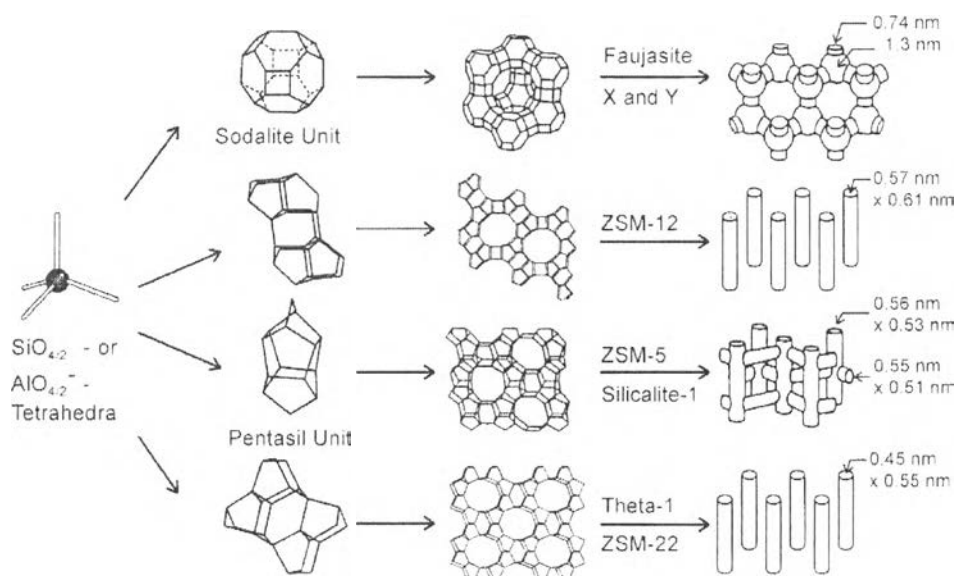


Figure 2.5 Examples of zeolite structure and their micropore systems and dimensions (Weitkamp, 2000).

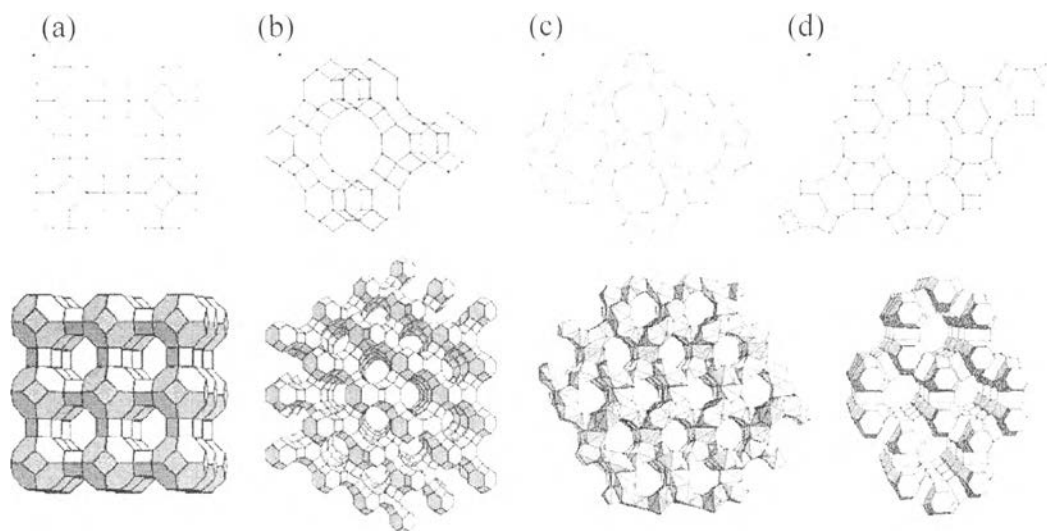


Figure 2.6 Zeolite frameworks (a) zeolite A (3D, 4.2 Å): (b) zeolite Y (3D, 7.4 Å); (c) zeolite L (1D, 7.1 Å): and (d) ZSM 5 (2D, 5.3 × 5.6 Å, 5.1 × 5.5 Å) (Zheng *et al.*, 2012).

A negative charge is introduced into the framework with each tetrahedrally coordinated aluminium Al^{3+} . This charge needs to be compensated by y/m cations A^{m+} , which are electrostatically bound to the host framework and mobile along the channels (Simon *et al.*, 1998). As a consequence, zeolites with high aluminum content are highly polar materials, potential ion conductors, and excellent ion exchangers. Furthermore, the aluminum ions act as highly acidic sites that can catalyze a number of chemical reactions. An important parameter for zeolites is the ratio of silicon to aluminum atoms in the lattice, x/y , which indicates the content of mobile cations as well as the amount of acidic centers per unit cell. In addition to their intrinsic components, zeolites can also be modified in a post-synthesis step by incorporating catalytically active metal clusters such as Pt, Fe, or Cu.

The unique properties of zeolites that make them attractive in the field of gas sensing materials are adsorptivity, high surface area, and porosity presence of mobile ions, and catalytic activity (Sahner *et al.*, 2008). Gas sensor devices based on zeolites can be divided into two major groups depending on the respective role of the framework material as shown in Figure 2.7. Zeolite can act as the main functional

element that relies directly on conductive, adsorptive, or catalytic properties of one specific zeolite and its interaction with the surrounding atmosphere. The second group encompasses devices using zeolites as auxiliary elements. This includes coated systems, sensitive material coated onto a zeolite and vice versa, as well as host-guest set-ups with the active materials encapsulated within the zeolite framework.

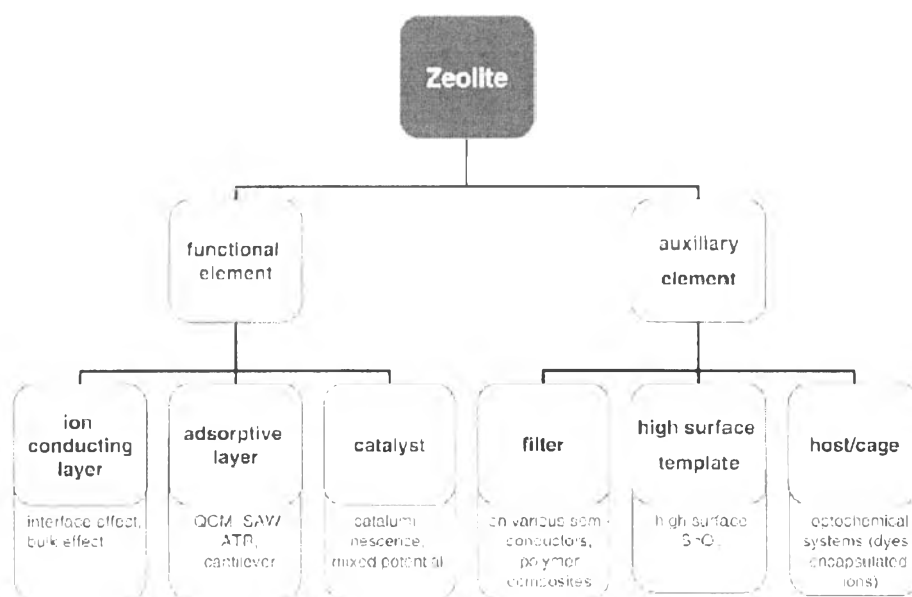


Figure 2.7 Classification of zeolite-based gas sensors (Sahner *et al.*, 2008).

2.2 Literature Survey

2.2.1 Sensors based on Conductive Polymers

Much attempt has been devoted to improve the sensitivity, response time and stability of gas sensors by modifying the sensing materials. An advantage of using a conductive polymer as the active material is that the chain structure of conductive polymer can be easily modified.

Torsi *et al.* (2004) studied dipentoxo substituted polyterthiophene thin films as active layers in organic thin-film-transistor device configuration, for using as alcohol sensing layers both in a thin-film-transistor (TFT) and in a quartz crystal microbalance (QCM) configuration. They found that the responses to 1-hexanol and

ethanol molecules are very fast: extremely reversible and the best extrapolated sensitivities are as good as 0.7 mg/ppm.

Melo *et al.* (2005) used the technique of polymerization in vapor phase to obtain different composite blends of PPy and other polymers such as poly(caprolactone) (PCP), poly(ethylene oxide) (PEO), poly(methyl-methacrylate), (PMMA), poly(vinyl alcohol) (PVA), and poly(vinyl acetate) (PVAC), and tested the corresponding sensitiveness towards the volatile compounds such as methanol, ethanol, carbon tetrachloride, and benzene. These polymeric blends were obtained in the form of films deposited on ITO substrates. The result showed the PMMA/PPy, PVA/PPy, and PVAC/PPy blends had a substantial increase in their conductivity after the exposures to the polar compounds methanol and ethanol. These blends showed a better level of recognition of polar compounds than that of the doped PPy films alone.

Aniline and pyrrole have been oxidized with ammonium peroxydisulfate in aqueous solutions, in the presence of equimolar quantities of hydrochloric acid. The effect of oxidant-to-monomer molar ratio on the syntheses of PANI and PPy was investigated (Blinova *et al.*, 2007). The yield of polymerization increased as the oxidant-to-monomer molar ratio increased from 0.2 to 1.5. The conductivity of the polymers was only slightly dependent on this ratio. The maximum conductivity of PANI was 4.0 S/cm at the oxidant-to-monomer molar ratio 1.3, and of PPy 0.3 S/cm at the ratio 1.1.

In 2008, the nanocomposites of leucoemeraldine base polyaniline (LEB-PANI), poly-vinyl-pyrrolidone (PVP), and cellulose acetate (CA) was developed based hybrid systems for selective room temperature detection of NO₂ (Haynes, 2008). The nanocomposites exhibited relatively high sensitivity and selectivity to NO₂ of 0.5 ppm, with response times of 40 sec, and recovery times of 155 sec under N₂ varying levels of humidity. Furthermore, DC electrical resistance measurements revealed that the responses of the LEB-PANI composites showed dependent on the humidity level and concentration of LEB-PANI. At low concentrations, the resistance decreased on exposure to NO₂. For a 1:1 PVP LEB-PANI ratio there was no response to NO₂, and for high LEB-PANI concentrations the resistance increased on exposure to the analyte.

A novel conductive polymer, poly(4'-hexyloxy-2,5-biphenyleneethylene) (PHBPE) was synthesized and used as the active layer of a selective gas sensor for dichloromethane, bromochloromethane, trichloromethane, tetrachloromethane, and 1,2-dichloroethane (Li *et al.*, 2008). The reasons for designing the PHBPE structure for this purpose was based on the following facts: (a) alkoxyated arylene oligomers have shown excellent sensing properties to VOCs; (b) alkoxy side chains enhance the solubility of CPs in organic solvents, important for film processing; (c) the polymer is a derivative of poly(*p*-xylylene) (PPX), a highly stable material, compared to conjugated polymers as, for instance, poly(*p*-phenylenevinylene) (PPV) since there are no double bonds between the arylene moieties that could be oxidized by air/humidity; and (d) although there is no extended conjugation through the polymer chain, the presence of biphenylene units (six conjugated double bonds) may ensure doping and electrical conductivity. The polymer was thermally resistant up to 185 °C. The electrical conductivity exhibited significant changes upon exposure to five vapors. The conductivity decreased after exposure to tetrachloromethane and increased after exposure to all others.

The composite fiber of camphorsulfonic acid (CSA) doped poly(*o*-anisidine) (POA)–polystyrene (PS) was produced in a non-woven mat form with different fiber characteristics for use as chemical vapor sensors (Aussawasathien *et al.*, 2011). The electrical resistance of the composite fiber decreased with increasing polarity of volatile chemicals. The sensitivity of the composite fiber sensor when exposed to water vapor was higher than that of the composite fiber sensor subjected to ethanol vapor due to high polarity together with low vapor pressure of water compared with those of ethanol. Moreover, the sensor could be reused several times without any change in sensing behavior and/or damage to the sensing materials.

2.2.2 Synthesis of Polydiphenylamine

In order to increase the thermal and oxidation stability of polyaniline without degradation of its conductivity, polydiphenylamine (PDPA) has been studied. Polydiphenylamine can be synthesized via chemical oxidative, electrochemical polymerization by a 4,4' C-C phenyl-phenyl coupling mechanism leading to a

structure with alternating amine and *p*-diphenylene units (Santana *et al.*, 1998; Hua *et al.*, 2003; Hua *et al.*, 2005; Li *et al.*, 2008).

PDPA can be synthesized directly in the doped form or easily doped with HCl solution to obtain polaron or bipolaron forms. PDPA show many properties that are not comparable with another polymer of N-substituted aniline derivative, these include electrochemistry, conductivity, and electrochromism (Dao *et al.*, 1989; Guay *et al.*, 1990).

Orlov *et al.* (2006) studied the chemical oxidative polymerization of diphenylamine via three mechanisms: (1) Polymerization in a solution of sulfuric acid, a 0.1 solution of diphenylamine in 5 M sulfuric acid (H_2SO_4) and a 0.125 M solution of ammonium persulphate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 5 M sulfuric acid (1/4 based on the total volume) were prepared. (2) Polymerization in a H_2SO_4 -*tert*-butanol mixture, a 0.2 M solution of diphenylamine in a mixture of 4 M H_2SO_4 and *tert*-butanol (equal volumes) and 0.25 M solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the same solvent (1/4 based on the total volume) were prepared. (3) Interfacial polymerization, a 0.2 M solution of diphenylamine in toluene and a 0.25 M solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the same volume of a 1 M solution of HCl were prepared. In order to start polymerization, solution of monomer and oxidizer were first cooled to $-2-0\text{ }^\circ\text{C}$ and mixed momentarily at a certain time interval, the reaction mixture was precipitated into either a 5-fold excess of ice water (polymerization in H_2SO_4 and the H_2SO_4 -*tert*-butanol mixture) or a 5-fold excess of isopropyl alcohol cooled to $-2-0\text{ }^\circ\text{C}$ (the interfacial polymerization), filtered, and washed many times with distilled water until the reaction was neutral. For polymerization in solution of H_2SO_4 , they found that the kinetic curves did not exhibit the S-shaped pattern as the typical kinetic curve polymerization of aniline, slow rate of polymerization, low molecular weight, and short induction time. But in the interfacial polymerization, they found that the kinetic curve exhibited the S-shaped and had higher molecular weight. Hence, they expected to use the interfacial polymerization for preparation of polydiphenylamine.

The PDPA film was fabricated via electrochemical polymerization and the spectroscopic characterization and stability of the diphenosemiquinone aminoimine and diphenosemiquinone diimine segment in the PDPA backbone were investigated (Santana *et al.*, 1998). The result indicated that the nature of the adsorbed

film was a function of the potential where the electrochemical synthesis was terminated. Comparing the in situ and ex situ spectra of the PDPA, it was possible to infer about the stability of the charged segments in the polymeric matrix. The excitation radiation at 524.5 nm induced the conversion of diphenosemiquinone aminoimine structure to diphenoquinone diimine and diphenyl diamine segments.

Wen *et al.* (2002) synthesized PDPA via electrochemical and chemical polymerization and then doped with 3 M methane sulfonic acid (MeSA). This study investigated the doping characteristic of PDPA through X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FT-IR), UV- visible spectroscopy and thermogravimetric analysis (TGA). PDPA prepared in MeSA possessed a peak at 167.9 eV in XPS spectrum for S, which signified the doped nature of the polymer. The presence of peaks at 1027 and 993 cm^{-1} corresponding to stretching of S_2O band also favored the doping of PDPA by MeSA. The observed doping level of 0.37 in MeSA was higher than noticed (0.25) with Et_4NBF_4 . The weight loss of 13% due to dopant removal as obtained from thermogravimetric analysis was consistent with a doping level of 0.37 (from XPS measurements) for PDPA. The redox characteristics of PDPA involving transitions from reduced PDPA structures to diphenosemiquinone imine and diphenoquinone diimine forms were evident from the presence of twin peaks in cyclic voltammogram and peaks at 380, 470, 570 and >750 nm in the UV-visible spectrum during electropolymerization.

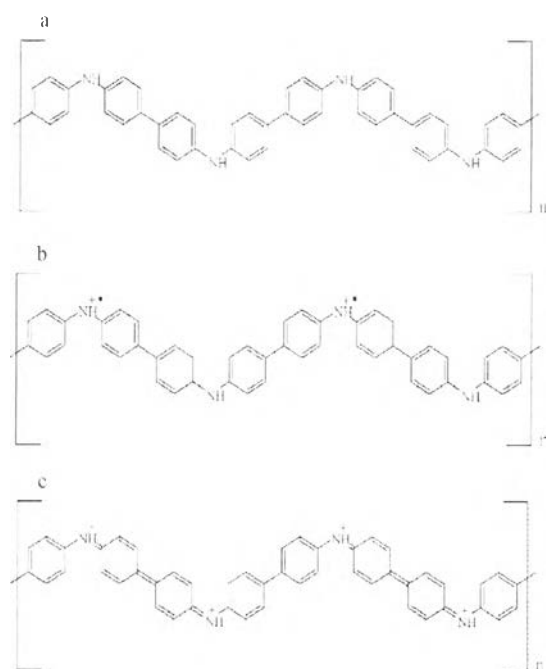


Figure 2.8 a) Neutral structure of PDPA; b) Polaron structure of PDPA; and c) Bipolaron structure of PDPA (Wen *et al.*, 2002).

Zhao *et al.* (2005) fabricated highly ordered PDPA via electrochemical polymerization using a porous aluminum oxide (AAO) template membrane. Owing to a larger pore size distribution in the AAO membrane, the polymer formed a continuous conducting chain within the AAO membrane. The result of TEM revealed that the obtained PDPA nanofibrils had uniform and well-aligned array with a diameter of 80 nm.

Santhosh *et al.* (2007) developed an amperometric sensor for CO gas from polydiphenylamine and multiwall carbon nanotubes composites. Polydiphenylamine was grafted on multiwall carbon nanotubes (MWNT-g-PDPA) on a glassy carbon (GC) electrode through electrochemical polymerization. Cyclic voltammetry was used to fabricate the modified electrode and to demonstrate the electroactivity of MWNT-g-PDPA toward gaseous CO. The MWNT-g-PDPA exhibited high sensitivity for oxidation of CO in a 0.5 M HClO₄ solution. The dependence of the response current on CO concentration was explored under optimal conditions and an excellent linear concentration ranged between 10 and 200 ppm with a substantially low detection limit of 0.01 ppm was obtained.

Santhosh *et al.* (2009) prepared hollow sphere nanostructure PDPA (HS-PDPA) through a "soft template assisted self-assembly" approach and used as a matrix for glucose biosensor. An enzymatic glucose biosensor was fabricated through immobilizing glucose oxidase (GOx) into HS-PDPA matrix. The amperometric current response of HS-PDPA-GOx to glucose was linear in the concentration range between 1 and 28mM with a detection limit of 0.05mM (S/N = 3). Also, HSPDPA-GOx electrode showed high selectivity towards glucose in the presence of ascorbic acid, uric acid and acetaminophen at their maximum physiological concentrations.

Massoumi *et al.* (2010) synthesized poly(diphenylamine-co-aniline) by electrochemical and chemical oxidative polymerization. The feed ratio of aniline and diphenylamine was varied under cyclic voltammetric conditions in aqueous sulfuric acid on the surface of the working glassy carbon electrode. The nano particle, and rod like pattern of poly(diphenylamine-co-aniline) was obtained from electrochemical, and chemical oxidative polymerization, respectively. The conductivity of the obtained copolymers with nano-particle morphology was approximately noticeably higher than that of the copolymers with rod like morphology.

Palaniappan and Manisankar (2011) synthesized polydiphenylamine by mechanochemical route and doped it with different dopants: HCl, H₂SO₄, and H₃PO₄ for used in hybrid supercapacitors. The H₂SO₄ was found to be the most suitable protonating or doping agent for polymerizing diphenylamine through this novel solid state route. The supercapacitor studies performed for the PDPA-H₂SO₄/AC cell revealed an excellent performance for the as prepared polymer and thereby indicated the successful application of mechanochemically prepared PDPA-H₂SO₄ as a cathode material in hybrid supercapacitors.

2.2.3 Zeolite

Shirazi *et al.* (2008) synthesized zeolite ZSM-5 with different Si/Al molar ratios in the range of 10-50 by using sodium silicate, aluminum sulfate and tetrapropylammonium bromide as the organic templates. SEM results showed that ZSM-5 synthesized with different Si/Al molar ratios had different morphologies and particle sizes. It was found that the average ZSM-5 crystal size increased as Si/Al molar ratio increased. The H-ZSM-5 acidity was determined by NH₃-TPD. These

results showed that different Si/Al molar ratios had an effect on the surface acidity of samples. The surface areas of the H-ZSM-5 were measured using BET method and the results showed that a decrease in Si/Al ratio decreased the surface area.

Zeolite ZSM-5 was dealuminated using mild dealumination process with HCl, acetylacetone, and ammonium hexafluorosilicate (Kumar *et al.*, 2000). Ammonium hexafluorosilicate could be the reagent most suited among the three reagents studied for dealumination of ZSM-5 to obtain maximum isomerization as well as *p*-xylene selectivity at optimum conversion. Moreover, the crystallinity slightly increased with increasing Si/Al ratio.

Dealuminated zeolite ZSM-5 used in ethylene oligomerization was investigated to study the role of Bronsted acid sites in the formation of higher hydrocarbons (Amin *et al.*, 2002). Both the zeolite and dealuminated zeolite ZSM-5 were characterized by FT-IR and XRD measurements. The FT-IR band at 1099 cm^{-1} attributed to the asymmetric stretching of framework Si-O-Si or Si-O-Al bonds showed a significant decrease in the intensity framework for the dealuminated samples. Dealumination time also affected the amount of aluminum in the zeolite framework; the dealumination time of 12 hr showed the highest Si/Al ratio.

2.2.4 Sensors based on Zeolite

Satsuma *et al.* (2011) investigated thick film zeolites, MFI, MOR, and BEA as multifunctional materials for detection of water, acetonitrile, ammonia, benzonitrile, pyridine, aniline, and triethylamine. The impedance spectra of the thick film zeolites showed a semicircle attributable to an RC parallel equivalent circuit from 4 Hz to 1 MHz, and resistance (R) decreased in the presence of 300 ppm of base molecules at 300 K. For smaller molecules having molecular diameter of less than 0.4 nm (water, acetonitrile, and ammonia), a good correlation was observed between the response magnitude of R and the proton affinity of base molecules. It was indicated that acid–base interaction was the major factor when molecular diameter was smaller enough than zeolite pore diameter. As for larger molecules (benzonitrile, pyridine, aniline, and triethylamine) of which the molecular diameter was nearly the pore diameter of zeolites, the response magnitudes were lower than those of smaller molecules.

Zeolites Y, 13X and AlMCM41, with the nominal pore sizes of 7, 10 and 36 Å, were used as the minor phases in fabricating polyaniline/zeolite composites (Densakulprasert *et al.*, 2005). The effects of zeolite content, pore size and ion exchange capacity on electrical conductivity response to carbon monoxide (CO) of polyaniline/zeolite composites were investigated. With an addition of zeolite 13X to pristine polyaniline, the electrical conductivity sensitivity to CO/N₂ gas increased with zeolite content. For the effect of zeolite type, the highest electrical conductivity sensitivity was obtained with the zeolite 13X, followed by the zeolite Y, and the zeolite AlMCM41, respectively. Poor sensitivity of zeolite AlMCM41 was probably due to its very large pore size and its lowest Cu²⁺ exchange capacity. Zeolite Y and zeolite 13X have comparable pore sizes but the latter has a greater pore free volume and a more favorable location distribution of the Cu²⁺ 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.

Electrical conductivity response of polyaniline/zeolite composites towards CO was investigated in terms of dopant type, dopant concentration, zeolite LTA content and zeolite pore size (Chuapradit *et al.*, 2005). Addition of zeolite 4A reduced the electrical conductivity response but improved the sensitivity towards CO with increasing zeolite concentration up to 40 %w/w. This concentration was evidently below the percolation threshold value, which was estimated to be above 50 %w/w. Composite with zeolite 3A had a comparable sensitivity value relative to that of pure polyaniline. Composites of 4A and 5A had greater sensitivity values over that of the pure polyaniline at the CO concentration range between 16 and 1000 ppm. Zeolite 5A was the most effective mesoporous material in promoting interaction between CO and polyaniline because of its largest pore size of 5 Å, relative to the zeolite 3A and 4A which had the pore sizes of 4 and 3 Å, respectively.

Thuwachasoan *et al.* (2007) investigated the electrical conductivity response toward H₂ of poly(3-thiopheneacetic acid), P3TAA and zeolites (zeolite L, mordenite, beta) composite. The composites showed negative electrical conductivity responses and sensitivity when exposed to H₂ relative to N₂ due to the weaker interaction between H₂ and the polaron or the bipolaron species relative to that of N₂. For effect of zeolite content, the composite with 20 %v/v of zeolite mordenite had the

highest electrical conductivity sensitivity value. The electrical conductivity sensitivity of all the composites increased with decreasing Al content because of a lesser interaction between H₂ and the zeolite.

Yimlamai *et al.* (2011) studied the electrical conductivity response of zeolite Y, ZSM-5, and mordenite towards ethanol vapor. Zeolite Y had a higher electrical conductivity sensitivity value than that of H⁺MOR because of a greater pore volume and available surface area. For the effect of the charge balancing cation, all NH₄⁺ ZSM-5 zeolites (Si/Al = 23, 50, 80, 280) showed negative responses, whereas the H⁺Y zeolites (Si/Al = 30, 60, 80) and the H⁺MOR zeolites (Si/Al = 30, 200) showed positive responses. These differing behaviors could be traced to the electrostatic field at the cation sites in zeolite micropores, and their hydrophilic–hydrophobic character, which affected the adsorption properties of the zeolites. For the effect of Si/Al ratio, the electrical conductivity sensitivity towards the ethanol decreased with increasing Si/Al ratio or decreasing Al content, and there was a lesser degree of interaction between ethanol molecules and the active sites of the zeolites due to its higher hydrophobicity and the lower amount of cations.

Chanthaanont *et al.* (2011) fabricated composite of poly(3,4-ethylenedioxythiophene), (PEDOT) doped with poly(styrene sulfonic acid), (PSS), PEDOT-PSS for used as carbon monoxide sensing materials. The electrical conductivity responses of PEDOTPSS/ ZSM-5 composites were altered due to the available adsorption sites for CO molecules. The electrical conductivity sensitivity to CO increased with decreasing Si/Al ratios. The addition of ZSM-5 zeolites to the pristine PEDOT-PSS improved the electrical conductivity sensitivity of the composites by enhancing the interaction between PEDOT-PSS and CO gases.