CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1 Theoretical Background

2.1.1 Gas Sensor Applications

Currently, the environmental pollution from various organic volatile compounds (VOC) is the most concerned topic in many countries. Because the production and usability process of petroleum and petrochemical products can release the volatile organic compounds or VOCs causing the pollution and harm towards human health. Additionally, VOCs are easily ignited in ambient condition. Most toxic gases and chemical vapors belong to a variety of groups such as carbon monoxide (CO), nitrous oxide (NO), organo-phosphate compounds, and other VOCs. Therefore, the development of sensor equipment is needed to monitor the safety limit of toxic gases and VOCs (Fanget et al., 2011). Table 2.1 and Figure 2.1 show the immediate dangerous to life or health (IDLH) concentration within 2 min of exposure with death, and PEL permissible exposure limit (PEL) concentration within 5 min of exposure with no errors or misclassifications from the World Health Organizations (WHO). Detection limits are generally well below the PEL (in most cases below 5% of PEL) and are typically in the low ppb range.

Table 2.1 The chemical molecular and the PEL (ppm) and IDHL (ppm) of toxic chemical vapors

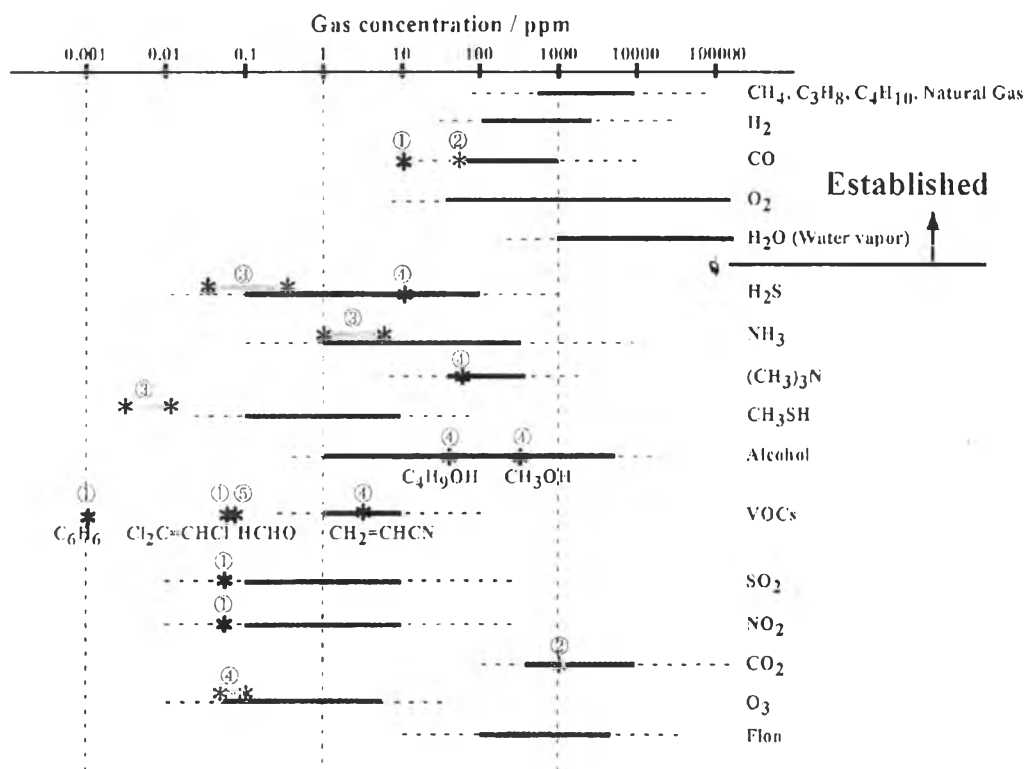| Gas/Vapor	Molecular Formula	PEL (ppm)	IDHL (ppm)
Ammonia	NH_3	50	300
Formaldehyde	CH_2O	0.75	20
Nitrogen Dioxide	NO_2	5	20
Sulfur Dioxide	SO_2	5	100

Figure 2.1 Concentration levels of typical gas components concerned. Star marks indicate the standards of the gases legislated in Japan by (1) environmental standard, (2) ordinance on health standards in the office, (3) offensive odor control law, (4) working environment measurement law, and (5) ordinance by ministry of health, labor and welfare (Yamazoe *et al.*, 2005).

Gas sensing technology has become more significant due to the concerning environmental topics in various areas such as industrial productions, medical applications, and environmental studies. Gas sensors are developed to detect the different types of toxic gases and most of them are ready to use in commercial markets. Gas sensors are of many types which can be classified by the method of detection as shown in Table 2.2 (Pandey *et al.*, 2012).

Table 2.2 Types of gas sensors based on detection method (Pandey *et al.*, 2012)

Type of Sensor	Gas Sensor	Detection Principle	Materials
Solid State Gas Sensors	Conductometric (conductivity impedance)	The conductivity changes during chemical vapor or gas exposure.	Metal oxides, conductive polymers, and porous materials
	Chemiresister	The resistance changes when exposure to chemical gas.	Metal oxides, conductive polymers, porous materials, and carbons
	Calorimetric	The concentration of combustible gas is measured by detecting the temperature rise resulting from the oxidation process on a catalytic element.	Pt, Au, metal oxides, conductive polymers, and porous materials

Table 2.2 Types of gas sensors based on detection methods (Pandey *et al.*, 2012) (continue)

Type of Sensor	Gas Sensor	Detection Principle	Materials
Solid Electrolyte Gas Sensors (Electrochemical)	Potenchiometry	Potentiometric sensors can measure electrical potential (voltage) change when exposed to gas and chemical vapors.	Metal oxides and conductive polymers
	Amperometry	Amperometric method produces current signal, which is related to the concentration of the analysis by Faraday's law and the laws of mass transport.	Pt electrode, Au-nafion, ceramics, metal oxides, and conductive polymers
Mass Sensitive Transducers (Piezoelectric Sensors)	Surface Acoustic Wave (SAW)	During gas exposure, the piezoelectric materials change in form of oscillation frequency.	Piezoelectric materials
	Quartz Crystal Micro Balance (QCM)	Change in frequency shift upon gas or chemical vapor exposure.	Piezoelectric materials
	Surface Plasmon Resonance (SPR)	Change in SPR signals is proportional to the refractive index close to the sensor surface and is therefore, related to the amount of bound gas molecule.	Piezoelectric materials

Table 2.2 Types of gas sensors based on detection method (Pandey *et al.*, 2012) (continue)

Type of Sensor	Gas Sensor	Detection Principle	Materials
Mass Sensitive Transducers (Piezoelectric Sensor)	Microelectromechanical Systems (MEMS) Based Sensors	The change of mechanical bending of micro- or nano-cantilevers when exposed to gas or chemical vapor adsorption of gas.	Metal oxides and conductive polymers
Optical Sensors	Spectroscopy	The optical techniques involve the absorption and emission spectrometry. The principle of absorption spectrometry is the concentration dependent absorption (molar absorptivity ε) of the photons at specific gas wavelengths.	Metal oxides, conductive polymers, and fluorescence dye

2.1.2 Gas Sensors Based on Conducting Polymers

The conducting polymer is one of materials used to develop chemical and biological sensors. Conducting polymers almost show no electrical conductivity in the neutral state. The induction of charges occurs through the doping process. This causes the polaron generation leading to the bi-polaron form as the electron is removed. The large change of conductivity occurs leading to various possible applications (Collin *et al.*, 1996).

In the chemiresistive sensor, the conducting polymers are well known due to the range of electrical conductivity near the metallic range. In the early stages, some conducting polymers were developed to detect VOCs by a swelling method. The swelling mechanism of well-doped conducting polymers is the separation between polymer chains or the distance for charge transport and the resultant electrical resistance (Bartlett *et al.*, 1996; Hangarter *et al.*, 2013).

Furthermore, the change in electrical conductivity relies on the change in optical properties in the near UV range. This is used for the electrochromic materials known as the photoluminescence sensors. In addition to the electroluminescence properties, electrochromic materials are used in electronic industry such as LED displays and smart windows.

The gas sensors based on conducting polymers have been utilized in detections of hydrocarbon vapors, fire, bacteria or fungi, water contaminant, chemical emissions in atmosphere, soil classification, light, and sounds as shown in Table 2.3 (Collin *et al.*, 1996).

Table 2.3 Gas and chemical sensors based on conducting polymers

Chemical Vapor/Gas	Conducting Polymer	Types of Sensor	Characteristics of Sensor	References
Acetone	Poly(aniline) (PANi)	Conductometric (conductivity impedance)	The conductivity changes during the acetone exposure and the detection limit is 29 ppm.	Do *et al.*, 2000
	Poly(pyrrole) (PPy)	Conductometric (conductivity impedance)	The conductivity changes by swelling and disorder effects.	Ruangchuay *et al.*, 2004
	poly(3,4-ethylene dioxythiophene) (PEDOT) nanowire	Chemiresistive	The detection limit is 1200 ppm and the resistivity increases with increasing the acetone vapor concentration.	Dan *et al.*, 2009
	Poly(EDOT-*co*-TAA) films	Conductometric (conductivity impedance)	These materials have selectivity to detect acetone vapor and the detection limit to acetone vapor is 10 ppm.	Vaddiraju *et al.*, 2010

Table 2.3 Gas and chemical sensor based on conducting polymers (continue)

Chemical Vapor/Gas	Conducting Polymer	Types of Sensor	Characteristics of Sensor	References
Methanol	Poly(pyrrole) (PPy) nanostructure	Chemiresistive	The PPy is highly sensitive and selective to methanol. It is capable for methanol determination in biodiesel samples.	Babaei *et al.*, 2013
Mixing VOCs Vapors (acetic acid, toluene, acetone, p-xylene, ethanol, 1-octanol, acetonitrile, and water vapors)	Poly(thiophene) (PTs) and derivatized	QCM	The QCM sensor has a high sensitivity to detect the low-polar or nonpolar vapor from mixing vapors. PTs coated on QCM exhibit good results ($r^2 = 0.99$) to predict toluene in a mixture of toluene and ethanol in the vapor mixing concentration from 0-20.000 ppm.	Si *et al.*, 2007

Table 2.3 Gas and chemical sensors based on conducting polymers (continue)

Chemical Vapor/Gas	Conducting Polymer	Types of Sensor	Characteristics of Sensor	References
Carbon Monoxide (CO)	Sulfonated poly(styrene) (PS)/poly(aniline) (PANi) composite film	Conductometric (conductivity impedance)	The nanocomposites films are excellent to detect CO gas. The resistivity of the film change at room temperature. After added TiO_2 into the composite system, the ability to adsorb CO increases reversibility even near room temperature (50 °C).	Ram *et al.*, 2005
Carbon Dioxide (CO_2)	Branched poly(ethylenimine) (BPEI) coated on poly(3,4-ethylenedioxythiophene) (PEDOT) film	Chemiresistive	BPEI layers are coated on the surface of PEDOT. The sensors show no response towards a pristine PEDOT layer and the response increases significantly to a value of 3.25% when adding a BPEI layer. The sensors show a higher response for CO_2 than for O_2.	Chiang *et al.*, 2013

Table 2.3 Gas and chemical sensors based on conducting polymers (continue)

Chemical Vapor/Gas	Conducting Polymer	Types of Sensor	Characteristics of Sensor	References
Ammonia (NH_3)	Poly(aniline) (PANi)/poly(methyl methacrylate) (PMMA) nanocomposite	Optical sensor	PANi-PMMA nanocomposite shows the optical property changes when exposed to the ammonia gas at the gas concentration of 10-1000 ppm and the adsorption activation energy is 0.3 ev.	Hu *et al.*, 2002
	Poly(aniline) (PANi)/TiO_2 nanocomposite	Chemiresistive	PANi/TiO_2 thin film shows a fast response (20-60 sec) and provides the stable (30 days), reproducible, and reversible resistance. They can adsorb NH_3 at the concentration of 23-141 ppm.	Tai *et al.*, 2008
	Poly(aniline) (PANi) nanowires (NWs)	Potenchiometry	The PANi-NWs particle diameters are from 50 to 200 nm and able to adsorb NH_3 at the concentration of 25–500 ppm. It exhibits the fast response time (36 sec).	Tuan *et al.*, 2012

Table 2.4 Sensing materials based on zeolites

Chemical Vapor/Gas	Metal Oxide and Porous Materials	Types of Sensor	Characteristics of Sensor	References
Acetone	Ag^+-ZSM-5 zeolite thick films	QCM	Ag^+-ZSM-5 shows high sensitivity and selectivity. The minimum detectable concentration of acetone vapor is 1.2 ppm with a fast response (90 sec).	Huang et al., 2004
Ethanol	Zeolitic films (MFI or LTA)	Chemiresistive	Zeolitic films (MFI or LTA) are coated on SnO_2 and used for gas phase sensing of different species (methane, propane, and ethanol). They show selectively higher response towards ethanol.	Mondel et al., 2011
Dimethyl Methylphosphonate (DMMP)	Zeolite ZSM-5 ion exchanged with Cu^{2+} (Cu-ZSM-5)	QCM	Nanosized Cu-ZSM-5 zeolites are used as a selective material for the detection of the nerve agent stimulant gas, DMMP. They show good selectivity and high sensitivity to DMMP vapor with a detection limit of 0.1 ppm and fast response (25 sec).	Ji et al., 2012

Table 2.4 Sensing materials based on zeolites (continue)

Chemical Vapor/Gas	Metal Oxide and Porous Materials	Types of Sensor	Characteristics of Sensor	References
Propane (C_3H_8)	Pt-ZSM-5 zeolite	Potenchiometry	ZSM-5 loaded Pt into the zeolite framework shows the selectivity towards propane when compared with Au-ZSM-5.	Dubbe *et al.*, 2008
	Na-ZSM with different Si/Al ratios	Potenchiometry	Na^+-ZSM-5 with a higher Si/Al ratio exhibits the higher sensitivities to propane at low concentrations (< 1000 ppm). The response time to adsorb propane decreases with increasing propane concentration.	Dubbe *et al.*, 2011
Nitrogen Dioxide (NO_2)	LTA and ZSM-5 zeolite	Chemiresistive	ZSM-5 zeolite has a selective response towards specific target gases by changing the cation in zeolite. H-ZSM-5 sensor has a response time towards NO_2 greater than other zeolites by a factor of 19.	Varsani *et al.*, 2011

2.1.3 Sensors based on Zeolites

The response of zeolites when exposed to various types of gas or chemicals vapor has been a subject of many studies with the emphasis towards the sensing applications. (Sahner *et al.*, 2008; Mori *et al.*, 2009; Li *et al.*, 2010; Jisa *et al.*, 2011; Lee *et al.*, 2011; Satsuma *et al.*, 2011). Gas sensor equipment based on zeolites has been divided in two major groups depending on the respective roles of the zeolite materials. The zeolites can act as the main functional element and they can use as the gas sensor based on the conductivity, absorptivity, and catalytic activities when exposed to the chemicals. Another group is an auxiliary element such as coating a zeolite on functional polymers and fillers.

Zeolite materials have been developed to be use in various sensor applications due to their unique characteristics: assembly of methyl blue for special sensing compound into zeolite framework for an oxygen sensor. Zeolites are plated on quartz crystal microbalances (surface acoustic-wave, micro cantilever, or optical fiber) for sensing some gases by selective absorption. The impedance measurement is one of techniques which use to monitor the conductivity change during the absorption of gases or vapors. Moreover, zeolites can be developed as filter materials for enhancing the selectivity of a certain gaseous molecules or into some materials or supports forming sensor composites as shown in Table 2.4 (Xu *et al.*, 2006).

2.1.4 Conductive Polymers

The conductive polymers are polymers containing the pi-conjugation or aromatic structures along the main chains such as poly(acetylene) or PA., poly(pyrrole) or PPy. poly(aniline) or PANi. poly(phenylene) or PPP, and etc. The conjugated polymers have alternating single or double carbon-carbon bond along the backbone. Most of the conductive polymers show no electrical conductivity in the neutral state and they are semi-conductors or insulators (Kumar *et al.*, 1998). The examples of conductive polymers neutral structures are shown in Figure 2.2
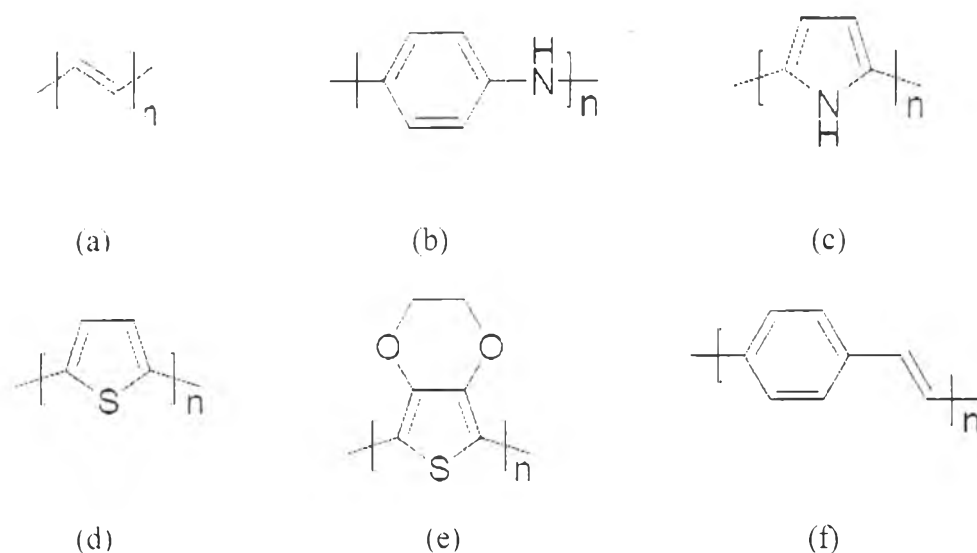
(a)　　　　　　　　(b)　　　　　　　　(c)

(d)　　　　　　　　(e)　　　　　　　　(f)

Figure 2.2 Typical conductive polymers in neutral forms: (a) poly(acethylene) ; (b) poly(aniline);(c) poly(pyrrole); (d) poly(thiophene); (e) PEDOT; and (f) poly(p-phenylene vinylene) (Kumar *et al.*, 1998).

The conductive polymers are synthesized via standard polymerization methods: Witting; Horner and Grignard reactions; condensation process; metal catalyst polymerization; and oxidative coupling with oxidizing Lewis catalyst leading to induce the aromatic block into the polymer main chain. The chemical polymerization is the most useful method to synthesize the conducting polymers. All conjugated polymers can be synthesized by this chemical polymerization (Kumar *et al.*, 1998).

Particularly, the conducting properties depend on the defects, chain length, and polydispersity index along the polymer molecules. In addition to the defects on the polymer structure, the conformation and linkage defects can significantly alter the structure by introducing the disorder or micro structure in the polymer. For the example, including the alkyl group and dioxyl group into poly(3-hexylthiophene) (P3HT) and PEDOT, the head-to-tail linkages of the copolymer are required for conjugation. The head-to-head or tail-to-tail linkages serve to decrease the electrical conductivity (Hangarter *et al.*, 2013).

2.1.5 Doping Process

The electrical conductivity of the conductive polymers can be enhanced by a method called doping process through adding a donor or a receptor along the polymer chain. Doing process is accomplished by a chemical method of direct exposure the conjugate structure to induce the charge transfer on the polymer structure. The charge occurs by a donated or withdrawn electron along the polymer backbone to obtain the polaron state via the oxidizing (p-doping) or reducing (n-doping) process. The process of charge formation is called "Doping Process" (Lange et al., 2008). For the n-typed doping process, the electrons are added to the conductive polymer chain to form the reduced state. In the former p-doping, when an additional electron is removed from the polaron state to another part of polymer backbone, the bipolaron state is obtained. The oxidation process or p-doping generates the positive charge at the conjugated backbone by adding the oxidizing agent as shown in Figure 2.3 (Shirakawa et al., 1971).
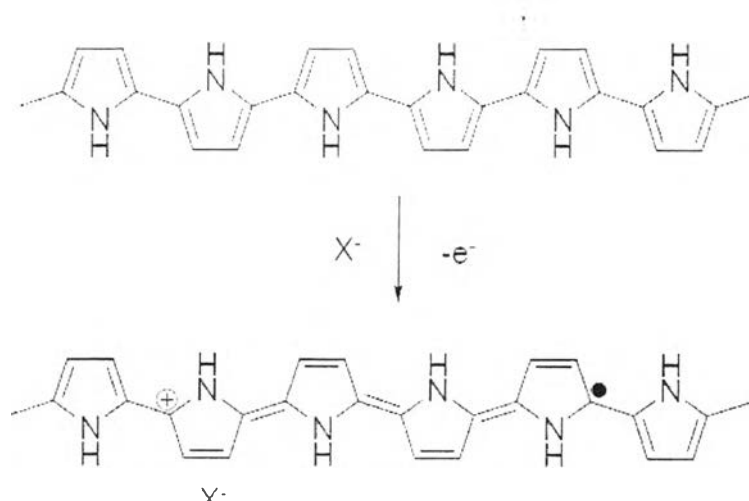

Figure 2.3 The oxidation process or p-type doping of PPy (Bai et al., 2007).

The conductive polymers may be doped by various techniques such as gaseous doping, solution doping, electrochemical doping, self-doping, radiated doping, and ion exchanged doping. The doping agents are either strong reducing or oxidizing agents which induce the neutral molecule to form ions. The properties of a

doping agent play a major role on the stability of conductive polymers (Kumar *et al.*, 1998).

2.1.6 Poly(p-Phenylene Vinylene)

Conductive polymer based on the poly(p-phenylene vinylene) or PPV structure is the most one of conductive polymer which is developed for various applications such as actuators, sensors, membranes, LED, and batteries. The structure of PPV is the combination between PA and PPP structure. They have many approaches to develop the method for PPV synthesis. Beginning, the Witig condensation or dehydrohalo-genation method is used to synthesize the PPV and results in the formation of oligomer. The Wessling-Zimmermann route is used to increase the molecular weight of PPV and development of the water soluble precursor (Lenz *et al.*, 1988).

The high conductivity of PPV was discovered, the doping process has been well studied. The neutral form of PPV has the specific conductivity in the range of 10^{-7}-10^{-8} S/cm. Upon the oxidative doping, the stable p-type doped PPV is formed with the polaron and bipolaron as the electron carriers along the PPV backbone and the specific conductivity of p-typed doped PPV is up to 10^{2}-10^{4} S/cm. The schematic of p-type doping mechanism is shown in Figure 2.4.
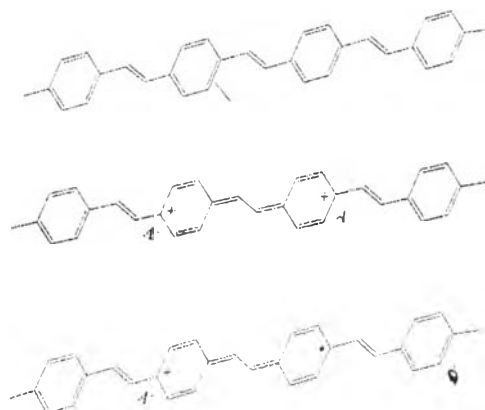

Figure 2.4 The schematic of p-type doping in PPV (Thongchai *et al.*, 2009).

The substituted functional groups on the PPV structure are the one of techniques which influences the electronic properties because of the inductive and resonant effects. For example, the effect of halogen substitution may cause the

intrinsic doping of the semi-conductive polymer. Because halogen can remove the electron from the aromatic ring which leads to decrease in the fluorescence of the molecules (Peres *et al.*, 2006).

Recently, PPV and its derivatives have been used to develop gas sensors or electronic noses. Although many materials have been used for this purpose, the use of PPV is an advantage to operate as the sensor at the ambient condition with fast response and high sensitivity than other materials. Additionally, PPV and other conductive polymers provide the unlimited possibilities of structural variations (Peres *et al.*, 2007).

2.1.7 The Interactions between Gas Molecules and Sensing Materials

The physical or chemical interactions between sensing materials and analyzed gases occur according to the natures of analyzed gases and sensing materials as shown in Figure 2.5.
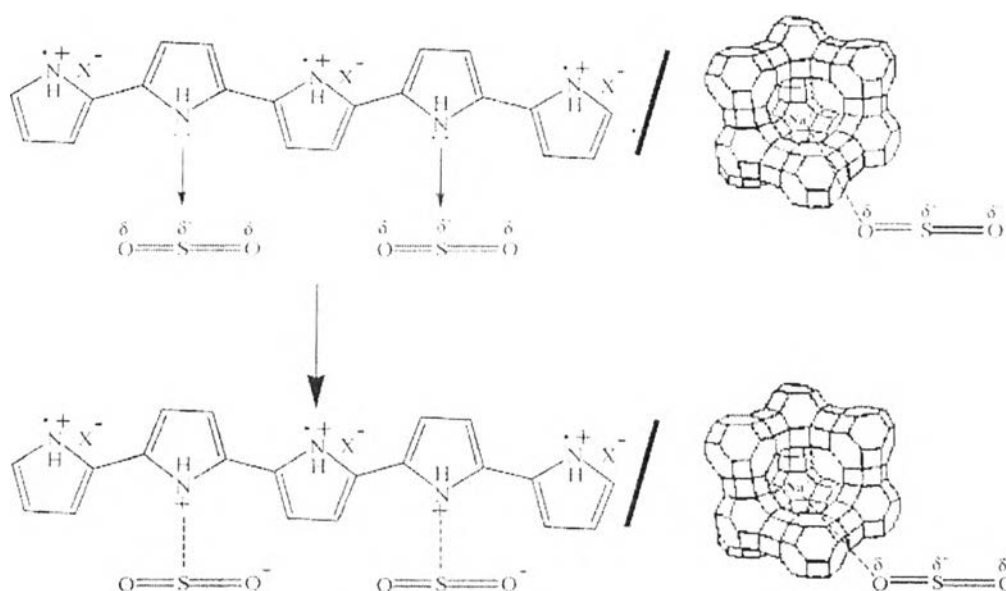

Figure 2.5 Interaction between Ppy/13X molecular sieve and SO_2 (Soontornworajit *et al.*, 2007).

The interactions between gases and sensing materials are chemical adsorption and physical interaction. The chemical interactions lead to a change in the level of doping along the conductive polymer and alter their physical and optical properties. For example: nitrogen dioxide (NO_2); iodine (I_2); trioxygen (O_3); and oxygen (O_2) can oxidize some conductive polymers and thus increasing the doping level (Voft *et al.*, 2000; Xie *et al.*, 2002; Bai *et al.*, 2007).

Some gases lead to a charge transfer rather than the redox or oxidation reaction. Carbon monoxide (CO) interacts with PANi in which CO withdraws the electron from the amine group along the PANi structure which in turn exhibits the positive charge on the carbon atom (Misra *et al.*, 2004; Dixit *et al.*, 2005).

Additionally, the composites between conductive polymers with metal oxides, carbon nanotubes, organic, and metal organic compounds provide the new analytical method (Ogura *et al.*, 1999; Hosseini *et al.*, 2003; Bai *et al.*, 2007). Ferrocene was immobolized on the PPy structure and improved the sensitivity of PPy towards CO gas. Radhakrishnan *et al.* (2007) proposed the mechanism that the CO molecule interacted with the iron ion on the ferrocene leading to a transfer of an electron to the PPY chain.

The interaction between VOCs compounds and conductive polymers are usually weak physical interactions. The adsorption of VOCs leads to a change the potential barrier along the polymer chain by the swelling process and the electrical resistance increases. Acetone is the one of the VOCs compounds in which the molecule diffuses along the PPy structure and destroys the hydrogen bonding interaction between aromatic PPy units. The disorder sections in PPy generate a longer distance between PPy structures thus hindering the electron mobility and decreasing the electrical conductivity of PPy under acetone exposure (Tan *et al.*, 2000; Ruangchuay *et al.*, 2004).

2.1.8 Zeolite

Zeolites are an inorganic compounds which are crystalline materials. They consist of hydrated aluminosilicates building block of group I and II elements, in particular, sodium, potassium, barium, and calcium. The structure of a zeolite is

typically in a framework structure which forms a three dimensional framework with linked channel systems where each channel is linked by sharing of oxygen. They are called meso or micro porous materials. The structures of zeolites are shown in Figure 2.6 (Auerbach *et al.*, 2003).
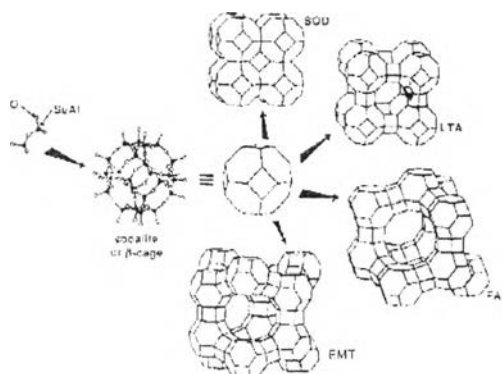

Figure 2.6 Four different zeolite structures (Sodalite, LTA, Faujasite, and ZSM) (Auerbach *et al.*, 2003).

Generally, the 3-D framework of one particular zeolite may be represented the chemical formula as $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$. In the oxide formula, x is mostly equal to or greater than 2, n is the cation valence. The framework is contained with the channels which are occupied by cations and water molecules. The negative charge is introduced into each channel and coordinated with the aluminium cation. This negative charge is needed to compensate with the metal cation having the electrostaticity with the framework. The zeolites with a high aluminum content are known as the highly polar materials or hydrophilic materials, ion conductors, or ion exchangers. The aluminum content corresponds to the acidic sites that can be utilized for the chemical reaction. Increasing the aluminum content in zeolites leads to the increase in the cation content within zeolite framework as the acidic sites. The cations are the part of mobile and are usually exchanged, at various degrees, by other cations (Breck *et al.*, 1973).

Because of the characteristic properties described above, zeolites are well known in a number of industrial applications. The major uses are in the catalytic bed in petrochemical industry, in the synthesis of chemicals in water purification,

and in the gas separation process. Other applications are in construction, agriculture, and etc. They are known as molecular sieves (Breck *et al.*, 1973).

Due to the porosity of zeolite materials which exhibit the property of sieves on the molecular scale. Breck *et al.* (1973) gave the other name of zeolite as the molecular sieves. Generally, zeolites have a pore size in range of 3-10 Å which is determined by the unit structure of the crystal. The pore sizes of zeolites are typically smaller than other porous materials such as clay. Due to the unique properties, zeolites are of high interest in the field of gas sensing. Figure 2.7 shows the comparison of the zeolite pore sizes with different framework structures. (Auerbach *et al.*, 2003)
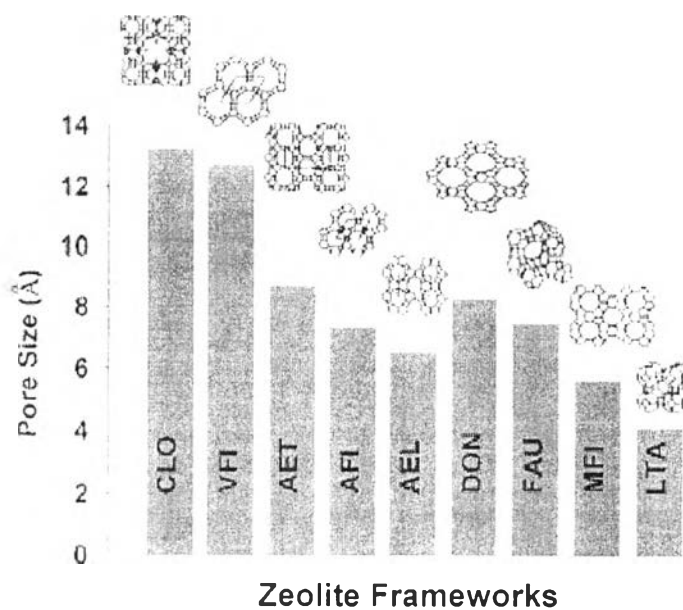

Figure 2.7 The Comparison of the zeolite pore sizes with different framework structures (Auerbach *et al.*, 2003).

2.2 Literature Survey

2.2.1 Poly(p-Phenylene Vinylene) and Doped Poly(p-Phenylene Vinylene)

The synthesis route of poly(p-phenylene vinylene) or PPV to get the high molecular weight had been developed by Wessling *et al.* (1967). This synthesis

route was started with α, α' dichloro-p-xylene and tetrahydrothiophene to prepare p-xylene-bis(tetrahydrothiophenium chloride) monomer. Then the polymerization reaction of this monomer was initiated by sodium hydroxide and poly((p-xylene)-bis(tetrahydro thiophenium chloride)) (PPV precursor) occurred. The precursor PPV was then changed to PPV via the thermal reaction at 180 °C. Generally, the molecular weight of polyelectrolyte was in the range of 10,000-1,000,000 g/mol.

The electrical conductivity of PPV depended on the molecular weight. The dopants used for PPV are iron trichloride ($FeCl_3$), triflic acid (CF_3SO_3H), sulfuric acid (H_2SO_4), and iodine vapor. Iodine (I_2) vapor was ineffective in doping PPV. The highest electrical conductivity of PPV was obtained from sulfuric acid and triflic acid and the electrical conductivity value was 10^4 S/cm indicating the metallic state, whereas iron trichloride showed the lowest electrical conductivity value (10^3 S/cm) (Ahlskog *et al.*, 1997).

Many of research works had been done on the doped PPV with iron trichloride. The structure of PPV showed the $FeCl_4^-$ form as a counter ion in the doped state. However, the doped PPV with iron trichloride had the lower conductivity than sulfuric acid and triflict acid. Kaneko *et al.* (1988) had noted that iron trichloride was of a faster rate in doping than sulfuric acid and triflict acid. Thus, a moderate doping rate and higher electrical conductivity values were likely to be obtained by using H_2SO_4.

Additionally, the substituting halogen group or the alkoxy group on PPV structure was one of the methods to enhance the performance of PPV in gas sensor applications. The PPV film, containing the bridged chain of dialkoxy (BDA) on the aromatic ring or PPV:BDA-PPV via the solvent and Langmuir-Blodgett (LB) method, and deposited on the gold electrode layer by layer. The sensing materials showed different responses to the variation of organic gases and vapors. The PPV:BDA-PPV film had a higher selectivity towards nitrogen dioxide (NO_2) gas when compared with the other gases: carbon monoxide (CO), nitric oxide (NO), ammonia (NH_3), and sulfur dioxide (SO_2). Thus, the modified PPV with the selective group along the polymer structure led to an improvement in the gas selectivity. The structure of halogenated and dialkoxy group on PPV structure was shown in Figure 2.8 (Babudri *et al.*, 2002).
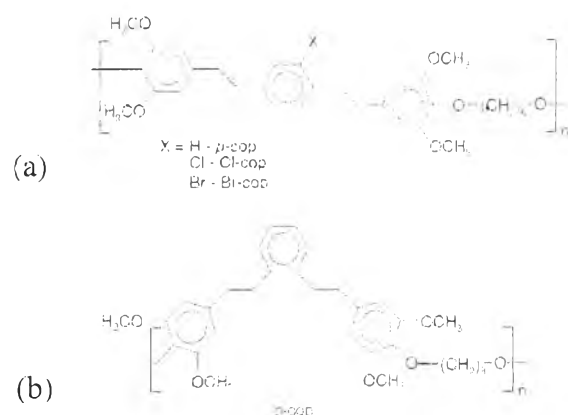
Figure 2.8 PPV structure as substituted by other selective groups: (a) halogen group (Peres *et al.*, 2006); and (b) dialkoxy group (Babudri *et al.*, 2002).

2.2.2 PPV and Other Conductive Polymers in Chemical Sensor Applications

Collin *et al.* (1996) developed a novel gas sensing detection system by using conductive polymers. PPy and PANi coated onto the poly(ethylene terephthalate) (PET) in nylon woven fabric form. The coating with the conductive polymers improved the selectivity of the target chemicals such as NH_3, DMMP, NO_2, and enhanced the sensitivity into the part per billion (ppb) regimes.

Prissanaroon *et al.* (2000) reported that PPy films doped with dodecylbenzenesulfonic acid or DBSA were used to detect small amounts of SO_2 in SO_2-N_2 mixtures. The short time conductivity response of the conducting films was improved at higher doping levels or by exposure to higher SO_2 concentrations. The gas sensitivity of a film given doping level, as measured by $\Delta\sigma_{dc}$ (electrical conductivity response), increased with SO_2 concentration. However, for a given SO_2 concentration, the gas sensitivity of the conducting films depended on the doping level. Below a critical doping level, the gas sensitivity is independent of the doping level. Above the critical doping level, the gas sensitivity rised sharply to a maximum and then slightly declined as the dopant concentration was increased. The results were interpreted in terms of the changes in the conducting film morphology from three-dimensional random coils to rod-like fibrillar structures.

The derivative of PPV or dialkoxy PPV which had the bridged chain of dialkoxy (BDA) on the aromatic ring of PPV was developed for gas sensor applications via the Langmuir-Blodget techniques (LB). The conductivity was changed when exposed to NO_2 at 75 °C. They also exhibited selectivity towards with NO_2 and no response to other gases such as CO (Babudri *et al.*, 2002). Redox reaction between the derivative of PPV and nitrogen dioxide increased the change of conductivity when exposed to NO_2.

Ruangchuay *et al.* (2004) attempted to improve the sensitivity of PPy towards acetone, toluene, water, and acetic acid vapor. PPy was blended with an insulating polymer such as PEO, PMMA, HDPE, PS, and ABS. The conductivity of the blends between PPy and insulating polymers was reduced by 1 to4 orders of magnitudes. The blends of PPy with PS, ABS, and PMMA showed significant responses towards acetone and toluene vapors due to the swelling effect.

Peres *et al.* (2006) prepared a doped block copolymer film containing PPV as a gas sensor. The polymer was tested with vapors of several organic solvents. The advantages of these sensors were as follows: (1) no sensitivity to water; (2) good reproducibility; (3) fast response; (4) durability of at least six months; (5) cheap and easy to make; and (6) ability to use separately in single-sensor solvent detectors or in arrays for electronic noses.

Li *et al.* (2008) studied and developed the novel of poly(p-xylylene) (PPX) and its derivatives. The derivative PPX polymer, poly(4-hexyoxy-2,5-biphenyleneethylene) (PHBPE) had a significant change in electrical conductivity during exposures towards five VHOCs (volatile halogenated organic compound): 1, 2 dichloromethane; bromochloromethane; tricloromethane; dichloromethane; and tetrachloromethane, and with a good selectivity. They found that the conductivity decreased with the exposure to tetrachloromethane and increased with the exposures to other VHOCs.

Jung *et al.* (2008) fabricated the nanostructure of the diblock copolymer pattern between PEDOT and polystyrene sulfonate (PSS) as an ethanol vapor sensor. The diblockcopolymer nanowire showed the high efficiency as an ethanol sensor comparing to the unpatterned film. In addition to the high sensitivity of the nanostructure patterned film, the sensitivity also depended on the film

thickness due to the improved surface area of the nanostructure to adsorb the high volume of ethanol vapor.

Benvenho *et al.* (2009) developed the copolymer between poly(2-bromo-5-hexyloxy-1,4-phenylene) and PPV as an ethanol detector in the ethanol-gasoline mixtures. They found that the copolymer exhibited the linear relation response of the ethanol concentration. The sensor could operate at the room temperature and could replace the lambda sensor in the flex-fuel vehicle.

The other detection methods, such as quartz crystal microbalance or QCM, were used to study the behaviors of the PANi thin film coated on the QCM electrode in detecting ethanol, methanol, 2-propanol, and 1-propanol. The frequency of the QCM electrode was changed due to the vapor absortion on the polyaniline thin film. The minimum concentration of methanol, ethanol, 2-propanol, and 1-propanol were 9, 9, 2, and 2 ppm, respectively. Increasing the thickness of PANi film could enhance the interaction between the alcohol and the conductive polymer due to the strong hydrogen bond formed at the main chain (Ayad *et al.*, 2009).

The PEDOT:PSS was modified as an electrode to monitor the nitric oxide gas by the drop-coated method which controlled the thickness of PEDOT:PSS. Lin *et al.* (2009) found that different volumes of the PEDOT:PSS drops controlled the porous structure and various of thicknesses and thus differeing responses towards the NO gas. The response of PEDOT:PSS increased with increasing thickness in the range from 2.3 um to 5.0 um during the NO exposure. However, at the low concentration of gas (10 ppm of NO gas), the response was not dependent on the surface area. The PEDOT:PSS showed the high response and was suitable to use at the ambient condition.

PPy nanowires were fabricated as a hydrogen (H_2) gas sensor by the technique of template-free electro-polymerization. The PPY nanowires, with the diameter in the range from 40 nm to 90 nm according to scanning electron microscopy analysis, were connected in the insulating gap between gold electrodes. The PPy nanowire sensor was used to detect with five concentrations of H_2 gas. These sensors exhibited a faster response relative to other structure types of PPy due to the high surface area of the PPy nanowire (Mashat *et al.*, 2012).

The thin film of derivatization of PPV which contained poly(20-dodecanoylsulfanyl-p-phenylene vinylene) and doped with DBSA was fabricated by a film deposition technique. The sensor exhibited the electrical conductivity change towards sugarcane mixed with methanol at the methanol concentration between 0.05% to 4.0% v/v (Peres *et al.*, 2012).

Boampong *et al.* (2013) modified the blended films of the conductive polymers between PANi and poly(ethyleneimine) (PEI) through spin casting. They investigated the formaldehyde detection through the changes in electrical conductivity. At the formaldehyde concentration of 38 ppm, the modified conductive polymer exhibited a significant response when exposed for 1 min. The films showed greater responses in formaldehyde than other volatile organic vapors such as methanol, acetone, and dichloromethane. The reason was because the acid doped PANi formed a nitrogen radical which provided the p-types doping. The formaldehyde molecules were able to accept the electrons from the doped polymer which led to a decrease in electrical conductivity.

The chemical oxidation-casting, chemical vapor deposition (CVD), and impregnated oxidation (IO) methods were used to synthesize PPy and PANi to detect acetone in a gas phase. The PANi showed the greater response to acetone vapor relative to PPy which was prepared by the CVD technique. The highest sensitivity and minimum response time were obtained with PANi prepared by the IO technique. The detection limit of acetone gas sensor based on PANi (IO) was 29 ppm (Do *et al.*, 2013).

2.2.3 Metal Oxide and Porous Materials in Chemical Sensor Applications

Dekker *et al.* (1989) studied the solid electrolyte as a hydrogen sensor by using the zeolite Y. NH_4^+ was obtained in zeolite Y (Si/Al=2.5 and Na^+) or NaY, the NaY was exchanged in 0.1 M NH_4Cl, and the HY was obtained by calcination of NH_4^+Y. The sensor was tested in a H_2 gas in the range of 0-100% mole of H_2 in N_2. The HY sensor had the fast response even at low temperature while NH_4^+Y showed the higher response than other types. Thus, NH_4^+Y zeolite was a potential candidate to be used as a H_2 sensor.

Some of research works developed zeolites with the layer of metal oxide to improve the selective and sensitive properties for hydrocarbon gas sensor (C_3H_8, C_3H_6, CH_4, H_2, CO, NO_2, and CO_2) by coating the zeolite film with Cr_2O_3 layer. The chromium oxide layer was coated between the layer ZSM-5 and gold electrode. The highest electrical conductivity was obtained in C_3H_6 whereas the lowest sensitivity was obtained in C_3H_8 at the vapor concentration of 250 ppm in N_2 gas. The sensor did not respond in other hydrocarbon vapors and the sensitivity was increased with increasing the hydrocarbon concentration. Therefore, the Cr_2O_3-ZSM5 was suitable as a hydrocarbon sensor due to the selective properties (Hagen *et al.*, 2006).

Yang *et al.* (2007) designed an efficient zeolite sensor for n-hexane. They showed the Lewis-base sites of zeolite are for the selective detection. The zeolite Y (Si/Al=2.5 and Na^+) or NaY and zeolite X (Si/Al=1 and Na^+) or NaX which beared large super cages were selective for n-hexane. Although the pore size of zeolite A (Si/Al=1 and Na^+) or NaA was matched with n-hexane, it could not form the four member ring and led to the low sensitivity when exposed to n-hexane. The NaY showed the highest sensitivity relative to other zeolite types. For the effect of alkalinity, the NaY and NaX were ion exchanged with Cs^+ and K^+. The basicity of cation was ordered as $Cs^+ > K^+ > Na^+$ due to the electronegativity values. Increasing the zeolite basicity reduced the electrostatic force between the zeolite framework and the cation which led to the increase in the interaction between n-hexane and the cation resulting in increasing the sensitivities of NaY and NaX towards n-hexane.

Moreover, the Ag-H-ZSM-5 zeolite was developed as the water vapor sensor at high temperature usage. The sensing detection method was UV spectroscopy which monitored the change in the adsorption band. The highly loaded silver particle in the ZSM-5 zeolite exhibited the adsorption band at 377 cm^{-1}. During water exposure with the presence the water molecule resulted in the erosion of the adsorption band at 377 cm^{-1} and the intensity of the band was fully recovered under water-free conditions. The optical properties of the Ag-H-ZSM-5 zeolite were stable under high-temperature treatment of zeolite under various conditions. Therefore, the zeolites which contained the metal particles were suitable to fabricate as a chemically/thermally stable sensing material under severe conditions. Moreover, the

other molecules in the gas stream, such as hydrocarbons, CO, and H_2 were affected on the formation of partial metal reduction. Hence, the metal modified zeolite was a candidate for use as a sensor especially in water vapor at high temperature (Sazama *et al.*, 2008).

In addition to zeolite being developed for gas sensor applications, metal oxides were also investigated to detect toxic gases and hydrocarbons. Mori *et al.* (2009) developed a potentiometric oxygen sensor to detect the several volatile organic compounds such as methyl ethyl ketone (MEK), ethanol, benzene, toluene, and ortho and para-xylene. The 8YSZ (8% Y_2O_3/ZrO_2) could detect the ethanol and MEK vapors at the vapor concentration of 1 ppm after modifying 8YSZ with the coated $SmFeO_3$ on the surface. The $SmFeO_3$ layer was formed on the fine particles on the Pt electrode and acted as the molecular selective and oxidative unit for VOCs. The oxygen absorbed on the surface of $SmFeO_3$ led to the reaction with hydrocarbon. They showed improved sensitivity of MEK and ethanol vapors by coating with $SmFeO_3$ while for other hydrocarbons there were no responses.

Li *et al.* (2010) modified the ZnO structure by the calcination of zinc hydroxide carbonate to form a multilayers nanosheet structure. The ZnO nanosheet could detect several hydrocarbon gases and vapors such as acetone, ammonia, ethanol, gasoline, methanol, and toluene. All gases were tested at 400 °C at the gas concentration of 100 ppm. The gas sensor based on ZnO multilayers nanosheet showed the enhancement of the gas response compared with the pristine ZnO nanoparticles due to high porosity of nanosheet morphology. In addition, the ZnO nanosheet exhibited the highest response when exposed to acetone vapor. The ZnO nanosheet was used to detect the acetone vapor in the range of 5-500 ppm. When exposed to acetone vapor at 5 ppm, the sensitivity was 8.67. With increasing acetone vapor concentration, the sensitivity increased. The response time and recovery time were important parameters in the gas sensing application. The ZnO nanosheet sensor immediately responded when exposed to acetone vapor at concentration of 100 ppm and other concentrations. For other hydrocarbon gases, same results were also obtained. The change of resistance was basically caused by the gas adsorption and desorption on the sensor surface. When exposed to air or oxygen, this resulted in an increase the potential barrier and a higher resistance. When exposed to the reduction

gas or vapor, the molecule of gas reacted with the oxygen molecule on the ZnO surface. This behavior resulted in a decrease in the sensor resistance.

Moreover, zeolites were developed for a toxic organophosphate nerve agent, DMMP, under the effect of cation types. The response of DMMP was investigated by impedance spectroscopy. The NaY was ion exchanged with NH_4^+, Li^+, Na^+, K^+, Cs^+, and TMA^+ and coated on the gold electrode. The change of impedance of NaY occurred when exposed to DMMP vapor in the vapor concentration range between 20 - 100 ppm. The cations with large sizes in the zeolite cages showed in higher impedance changes when exposed to DMMP due to the repulsive interaction between Si-O-Al of the zeolite cages and the cations leading to the increase in the ionic mobility. When CsNaY was exposed to CO, NH_3, C_3H_8, CH_4, and DMMP, it showed the highest sensitivity value when exposed to DMMP at vapor concentration of 100 ppm. For other gases, it could detect at the vapor concentration of 1000 ppm as the minimum vapor concentration. Thus, the sensor based on the zeolite Y showed the selectivity to the DMMP when compared with CO, NH_3, and other hydrocarbon gases and vapors (Li et $al.$, 2010).

The effect of acidity and pore diameter of zeolite on the response of water, acetonitrile, ammonia, benzonitrile, pyridine, aniline, and triethylamine were investigated by Satsuma et $al.$ (2011). Acidic zeolites namely MFI, BEA, and MOR were investigated. The sensitivity to NH_3 depended on the type of zeolite as the size of MOR > MFI > BEA, respectively. For small base molecules, the acid-base interaction was a factor on the sensitivity of the zeolites. In the case of large base molecules, such as pyridine and triethylamine, another factor on the sensitivity of the zeolites was the pore size. .

A metal oxide, (WO_3), was developed to detect NO_2 and CO through adding an acidic zeolite LTA and zeolite ZSM5 layers on the surface of WO_3. The effects of the zeolite layer, zeolite type, and cation type were investigated. The WO_3 modified with Cr-LTA zeolite had the highest sensitivity value of 3.5 when compared with H^+LTA when exposed to CO. The WO_3-Cr-ZSM5 possessed the sensitivity value of 8 when exposed to NO_2 in the concentration range of 95-400 ppb. Therefore, the acidic zeolites coated onto the WO_3 improved the responses of WO_3

when exposed to NO_2 and CO, and it was suitable to be used as a part of electronic nose (Varsani *et al.*, 2011).

Another sensing material, Si cantilever, was modified by coating with zeolites (NaA, HY, and MFI) or polymers poly(ether urethane) (PEUT), poly(epichlorohydrin) (PECH) and poly(isobutene) (PIB) to detect ethanol or toluene in the concentration range of 250-4000 mg/m^3. The results showed that Si catilevers coated with NaA, HY and MFI had higher sensitivity values than that of the PEUT coated Si cantilever under ethanol vapor. In the toluene exposure, the polymer coated Si cantilevers had higher sensitivity value than those of the zeolites. The NaA and HY coated Si cantilevers could detect ethanol and toluene vapors below 24 ppm and 26 ppm, respectively. On the other hand, the polymer coated Si cantilevers had the detection limit at 263 ppm in ethanol and 28 ppm in toluene. Thus, the zeolites could improve the cantilevers for gas sensing application (Urbiztondo *et al.*, 2012).

Ji *et al.* (2012) developed the ZSM zeolite for DMMP detection. Na^--ZSM-5 was exchanged with Cu^{2+} for different Cu^{2+} amount and coated on a quartz cryatal microbalanced (QCM) film in order to study the effects of Cu^{2+} concentration and DMMP concentration. The ZSM-5 with the highest concentration of Cu^{2+} exibited the sensitivity detection limit of 0.1 ppm towards DMMP vapor. The result suggested that the sensitivity increased in proportion to the copper cation content.

Recently, a metal oxide, namely Y, was used to dope an organic framework-5 (MOF-5) via a solvothermal (a synthesis method for growing single crystals from a non-aqueous solution in an autoclave (a thick-walled steel vessel) technique at high temperature (400 °C) and pressure) to use as a gas sensing material based on catalumine scence (CTL). The Y doped MOF-5 could detect iso-butanol at the vapor concentration of 3.7 mg/L and exhibited a linear response in the vapor concentration range from 6.4 to 80.1 mg/L. The CTL sensor type based on Y-doped MOF-5 showed weak efficiency to other volatile organic compounds. Additionally, Y-doped MOF-5 exhibited a higher response to iso-butanol than pure MOF-5 under the same conditions (Wan *et al.*, 2014).

2.2.4 Conducting Polymer/Porous Composites in Gas and Chemical Vapor Sensor Applications

The research works were composite materials gas sensors consisting of zeolites and conducting polymers based on the gas absorption properties of zeolites and the high electrical conductivity of conductive polymers. Chuapradit *et al.* (2005) attempted to improve the CO sensor of PANi by adding the zeolite LTA into the PANi matrix. Adding the 4A zeolite into the PANi, the electrical conductivity sensitivity increased with increasing 4A zeolite content up to 40% v/v. The composite materials with 3A zeolite as a filler had comparable sensitivity values with the pure PANi. The composites containing the 4A and 5A zeolites at a fixed zeolite content at 20% v/v had the highest sensitivity towards CO gas in the concentration range of 16-1000 ppm due to the effect of pore size. 5A zeolite had the suitable pore size to interact with CO gas. For the effect of dopant, hydrochloric acid (HCl) was effective more than maleic acid (MA) for using as a dopant.

Densakulprasert *et al.* (2005) studied the effects of zeolite content, pore size, and cation exchange capacities on the electrical conductivity response towards CO of PANi/zeolite composites. Zeolite Y, 13X, and MCM41, all having the Cu^{2+} as a common cation were dried and mixed with MA-doped PANi. The electrical conductivity sensitivity was obtained in this order 13X > Y > MCM41 due to the factor of pore size. MCM41 had the largest pore size so it was not favorable to adsorb the CO gas. The temporal response time increased as the amount of zeolite was increased.

Soontornworajit *et al.* (2006) studied the electrical conductivity sensitivity of PPy/molecular sieve 13X composites exposed to CO, CO_2, and SO_2 gases. The effects of cation type, cation content, and cation concentration were investigated. PPy and its composites showed negative responses towards CO and CO_2 gas but the positive response was obtained with the SO_2 exposure. Undoped PPy and doped PPy composites at 10% v/v of 13X zeolite showed the highest sensitivity to SO_2. For the effect of cation types, the PPy/Na^+13x composite had the highest sensitivity towards SO_2 whereas other composites containing other alkaline cations (Cs^+, K^+, and Li^+) possessed sensitivity in this order: Na^+ > Cs^+ > K^+ > Li^+.

Thuwachaosoan *et* al. (2007) studied the effect of zeolites L, mordernite (MOR), and beta (BEA) mixed with PEDOT to form composites as hydrogen sensing materials. For the effect zeolite type, the composite with 20% v/v of BEA zeolite had the highest sensitivity due to the lowest amount of Al. The induction time increased with increasing the amount of Al due to the greater available sites of positives charge on the polymer chain. The composites contained the MOR zeolite was ion exchanged from Na^+ to Li^+ and K^+ forms. PEDOT/Li^+-MOR showed the lower sensitivity than the composites containing MOR in K^+ and Na^+ due to the higher electronegativity and smaller radius of the cation.

Thongchai *et al.* (2009) attempted to improve a CO gas sensor via adding doped PPV into the zeolite matrix. The sensitivity of dPPV/Cu^{2+}-ZSM-5 showed the negative response of -0.154 while the composite containing Na^+ in the system showed the positive response of 1.48. The positive response of dPPV/Na^+-ZSM-5 was due to the interaction of CO acting as a secondary dopant.

Wannatong *et al.* (2008) fabricated the PPy composites containing zeolite 3A and polyamide to detect four chemicals in in lacquers. The composites were formed in two types (film and fiber bundle) and the electrical conductivity response was investigated under exposures to four organic vapors: acetone, MEK, methanol, and toluene. The composite containing 50% v/v of zeolite 3A and 20% v/v of polyamide in the PPy matrix in the film form showed the highest response towards methanol relative to other chemical vapors. Whereas the composite in the fiber form was not responsive to any of the chemical vapors as PPy particles were too far from each other in the bundle fiber form leading to low electrical conductivity response when exposed to the chemical vapors.

Arvand *et al.* (2011) prepared the composite between zeolite Y and polythiophene (PTP) by chemical oxidative polymerization of thiophene (TP) in the presence of zeolite Y (powder) in $CHCl_3$ solvent using the $FeCl_3$ as an oxidant. The PTP/zeolite Y composite showed a response towards sulfide ion in the pH range from 5 to 9. The composite electrode showed a high selectivity towards sulfide ion in the presence of other anions.

The fabrication of PANi and porous materials (Cu_2ZnSnS_4 or CZTS) thin film as a high performance LPG sensor was developed by Shinde *et al.* (2012).

The PANi/CZTS composite was synthesized from the layer by layer deposition of CZTS followed by electro-deposition of PANi. The structure of PANi/CZTS was of a nanostructure form. This sensor type showed the LPG response at the LPG concentration varying from 44% to 0.6% v/v. The composition of LPG gas was CH_4, C_3H_8, and C_4H_{10}; this molecule could reduce the hydrogen on the carbon atom and leading to a decrease in the barrier height for electron jumping and a response was obtained during LPG exposure. The PANi/CZTS composite showed good stability, fast response, and recovery time periods.

Chantaanont *et al.* (2012) prepared the composite between PEDOT-PSS and ZSM-5 zeolite to detect CO gas. The PEDOT was doped with poly(styrene sulfonic acid) or PSS and blended with ZSM-5 of the different Si/Al ratio. The electrical conductivity response of PEDOT-PSS/zeolite changed when adsorbing CO molecules. The electrical conductivity response of PEDOT-PSS/zeolite increased with decreasing Si/Al ratio. This was because the amount of cations present increased with decreasing Si/Al ratio leading to an increase in the active sites on the zeolite frame work.