



CHAPTER I INTRODUCTION

Air pollution, both indoors and outdoors, is a major environmental health problem affecting developed and developing countries alike. Its main sources are dust, gases, and smoke, as generated mainly by human activities as well as natural sources. When inhaled, air pollutants affect directly both lung and respiratory tract and they can also be taken up and transported by the blood streams throughout the body. Through deposition in the environment, air pollutants can also contaminate food and water. Gaseous air pollutants are principally oxides of nitrogen (NO_x), ozone (O_3), carbon monoxide (CO), sulphur dioxide (SO_2), ammonia (NH_3) and volatile organic compounds (Brett B.M., 1987).

Table 1.1 The guide line value for common pollutants

Pollutant	Annual ambient air concentration ($\mu\text{m}/\text{m}^3$)	Guideline value ($\mu\text{m}/\text{m}^3$)	Concentration at which effects on health start to be observed ($\mu\text{m}/\text{m}^3$)	Exposure time
CO	500-7000	100 000	Not applicable	15 min
		60 000		30 min
		30 000		1 hour
		10 000		8 hour
NO ₂	10-150	200	365-565	1 hour
		40		1 year
O ₃	10-100	120	Not applicable	8 hour
SO ₂	5-400	500	1000	10 min
		125	250	24 hour
		50	100	1 year

The rapid expansion of industries has induced greater concerns on public health and environment. Better process design, proper combustion unit or even effective waste recovery can lead to a better control for the emission of gases. Therefore, an effective tool to monitor the release of these gases or a gas sensor is desirable. There are several types of gas sensors: electrochemical, infrared, catalytic bead, photoionization and solid-state. The most widely used gas sensor is made of a metal oxide such as SnO₂ or ZnO. However, they have many disadvantages, the lack of sensitivity and selectivity at low concentrations, and the requirement in many applications to be operated at 300 °C or above (Garder *et al.*, 1994).

Conducting polymers have a potential to respond to a wide range of gases and in particular toxic gases. It can be operated at room temperature. However, conducting polymers lack sensitivity and selectivity to particular gases at low concentration (Conn, 1998).

Zeolite is a polycrystalline, microporous material with nearly uniform pore size distribution. It has been the subject of many recent theoretical and experimental studies as a gas adsorption material amongst its several applications (Dyer, 1998). The adsorption force of zeolite depends on the pore type, the pore size distribution, location, quantity and class of ion exchange cations.

1.1 Conductive Polymer

Conductive polymer was discovered more than 50 years. Polyacetylene was the first electrically conducting polymer, which was synthesized and discovered in 1977. The electronic conduction characteristics are caused by the π -conjugated system, which is formed by the overlap of p_z orbitals and alternating carbon-carbon bond length. (Kohlman, R.S., *et al.*, 1989). The system provides a pathway for electrons to migrate along a polymer chain and to jump from one chain to another chain.

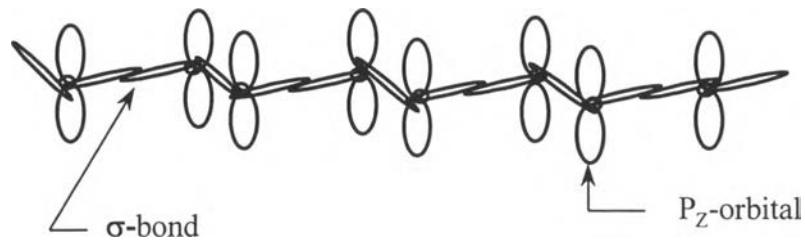


Figure 1.1 Conjugated system of a conductive polymer.

Presently, there are several families of conducting polymer such as poly(1,6-heptadiyne), polyaniline(PANI), polypyrrole(PPy), polythiophene(PT), poly(*p*-phenylene)(PPP), poly(*p*-phenylene vinylene)(PPV), and etc. The conductive properties of these polymers arise from the doping process. Doping process of a polymer can be carried out electrochemically or by exposing the polymer to a vapor or a solution consisting of a dopant. There are 2 different routes in the doping process; a dopant accepts charges (*p*-type) or donates charges (*n*-type) onto the polymer backbone.

Because of the unique properties of conducting polymers, they are used in a wide range of applications. In the past, conducting polymers have been proposed for uses as conducting wires, in batteries, light emitting diode, as electromagnetic interference shielding materials, sensor, and etc. (Trivedi, 1997).

1.2 Polyaniline

Polyaniline (PANI) has emerged as one of the most promising conducting polymers because it is an inexpensive monomer, relative ease of synthesis, good environmental stability and moderately high value of dc conductivity, and the excellent chemical stability in conductive form (Stejskal *et al.*, 1996). Polyaniline was first made in 1962 by H. Letheby and is called 'aniline black' (Barici *et al.*, 1996). It was introduced as a conductive polymer in 1977 by MacDiarmid and coworkers through its chemical structure (Cao *et al.*, 1989). It can be synthesized

either electrochemically giving a cohesive film, or chemically by an oxidative polymerization of aniline in aqueous acid solution (Huang *et al.*, 1986).

Polyaniline can be classified into 4 different oxidation states by the variation of oxidation level (Stejskal *et al.*, 1996). The first one is the pernigraniline form ($x = 1$), which is fully oxidized, providing a violet color. The second one is the emeraldine base form ($x = 0.5$) which is a general state of polyaniline with a dark blue color. The third one is the leucoemeraldine base form ($x = 0$), which is a fully reduced material with a yellow color. The last one is the polyaniline salt, which possesses a green color.

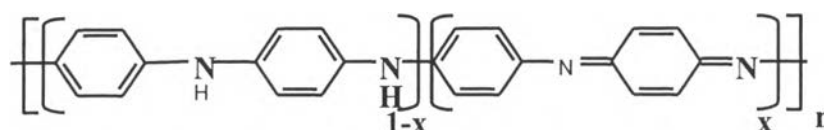


Figure 1.2 The polyaniline structure.

Two independent doping routes to create an emeraldine salt from an emeraldine base; by an oxidation either electrochemically or chemically, and by protonation through acid-base (Salaneck, 1993). It is normally accepted that protonation of polyaniline leads to the formation of radical cation by an internal redox reaction which causes the reorganization of electronic structure to give two semiquinone radical cations, called polaronic states (Dhawan *et al.*, 1997). The degree of protonation and following electronic conductivity thus become a function of pH (Salaneck, 1993). Oxidation causes a change in the total number of π electrons on the conjugated chains, while a protonation causes no change in the number of π electrons.

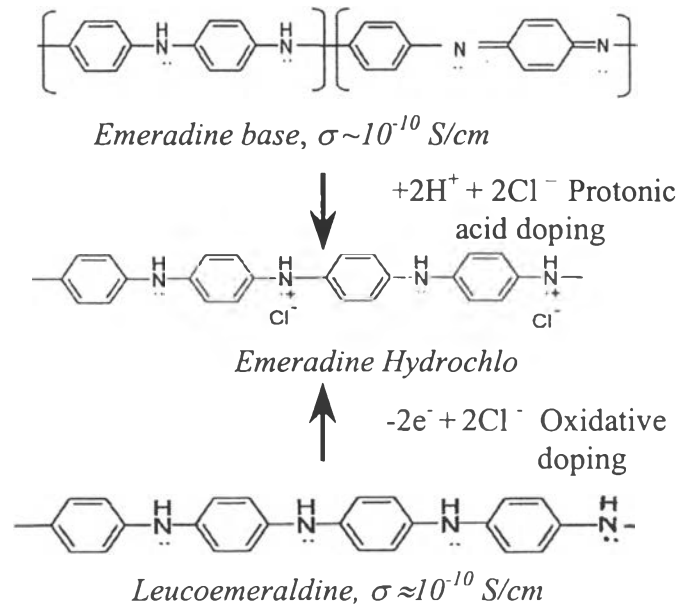


Figure 1.3 Protonic acid doping and oxidative doping of polyaniline.

1.3 Zeolite

Zeolite is a hydrate aluminosilicate minerals which was discovered in 1756 by a Swedish mineralogist, Cronstedt (Dyer, A., 1988). It was found in relatively small cavities (vugs) in rocks of a volcanic origin. Three-dimensional structures of zeolite arising from a framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ coordination polyhedral (Fig.3) is linked by all its corners. The frameworks generally are very open containing channels and cavities in which are located cations and water molecules. (Dyer, A., 1988)

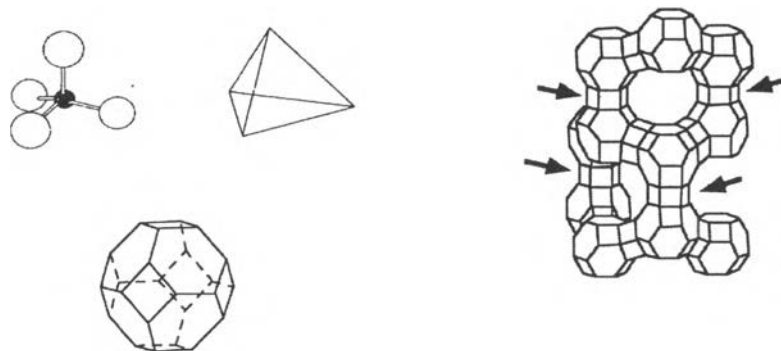


Figure 1.4 a) Tetrahedral structure $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$, b) sodalite cage, and c) Framework Zeolite Y.

The use of microporous material such as zeolite in catalysis and separation process is widespread in the petroleum and chemical processes. Due to the size- and shape-selectivity of zeolite crystals and their Lewis and Bronsted acid sites, zeolite plays a very important role in the molecular sieving selectivity. At present, large-scale applications are air separation, gas purification, drying agent, water treatment, odor control, industrial gas separation, and reinforcement filler (Dyer, A., 1993). In early works, zeolite was used as template synthesis of polyaniline to produce nanocomposite device (Wu, 1994 and Frish, 1996). Later, it was used as an ethanol filtering material, it was coated above a CO sensing layer to reduce a high sensitivity towards C_2H_5OH (Fukui and Nishida, 1997).

In this work, we shall report the electrical conductivity and sensitivity of PANI and PANI/Zeolite composites as CO sensors. We investigated the effects of dopant type and content on the electrical conductivity and sensitivity of PANI, and the effects of zeolite type and content on the electrical conductivity and sensitivity of PANI/Zeolite composite as CO sensor.