CHAPTER I
INTRODUCTION

1.1 Introduction

Presently, our environment contains several toxic gases quite dangerous to human beings. They are produced from many sources: hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and hydrocarbon gases are produced from petrochemical industry; carbon monoxide (CO), nitrogen monoxide (NO) and carbon dioxide (CO_2) from vehicle exhausts. Especially, carbon monoxide can create the dangerous effect of a low-level CO exposure: the binding with hemoglobin, producing a carboxyhemoglobin and the decrease in the oxygen-carrying capacity of blood. Due to increasing amounts of these toxic gases released, the requirements for better process control, new generations or improved gas sensors are desired. Normally, gas sensor devices use metallic oxides such as SnO_2 or ZnO as sensing materials. However, they required operating at 300°C or above (Miasik, 1986). Polyaniline, one of many conducting polymers, has a potential to respond to a wide range of gases and in particular toxic gases in addition to the ease of processing. Polyaniline could be operated at room temperature. However, polyaniline lacks sensitivity and selectivity to CO at low concentration (Conn, 1998) so that many researchers have developed a new type of polyaniline sensing composite materials. The combination of unusual and valuable properties of the polymer made them irreplaceable in many applications. For example, previous workers have used metallic oxides to improve selectivity of polyaniline for detecting combustible gas.

In gas separation and gas purification field, zeolite molecular sieves are well known for a wide variety of applications, particularly in their superior selective adsorption properties. Their properties can be chosen to be suitable to adsorb CO gas, which is our target gas.

1.2 Background

1.2.1 <u>Conductive Polymer</u>

Conductive polymer is a novel class of polymers that possesses higher electrical conductivity than ordinary polymers that are usually insulating materials. Electrically conducting polymers display the extended π-electron conjugation. The incorporation of the conjugation along the backbone is of foremost importance (Mark *et al.*, 1996) because it provides a pathway for electrons to migrate along a polymer chain and to jump from one chain to another chain. To convert an insulating polymer to a conductive polymer, charge transfer agents, dopants, are often required to inject electrons into the delocalized framework or to remove electrons and leave positive holes (Allcock *et al.*, 1990).

The conductivity, σ, is proportional to the product of the free-carrier concentration, n, and the carrier mobility, μ, as follow Equation 1.1:

$$\sigma = ne\mu \qquad (1.1)$$

where e is the unit electronic charge, 1.6×10^{-9} sec.A (Smith, 1974). n is number of carrier per unit volume, and μ is the carrier mobility, (cm^2/sec.volt).

The key properties of a conjugated polymer in relation to its potential as a precursor to conducting electrons are *ionization potential, electron affinity, band-width,* and *band gap.* Low value of ionization potential and high electron affinity indicate that a polymer can be easily oxidized (p-doping) and reduced (n-doping), resulting in increases in the carrier concentration, n, and electrical conductivity. The bandwidth indicates whether the ionized material is conductive to the intrachain charge transport and hence a large band-width is preferred. Although a conjugated polymer has a backbone structure well suited to electron conduction but conductivity is negligibly low since the conjugated polymer may have a relatively large band gap, so the concentration of free carriers, n, is very low at normal temperature. In addition, the electron transport properties of conducting polymers are

highly dependent upon the structure disorder, doping procedure, and aging (Skotheim *et al.*, 1998).
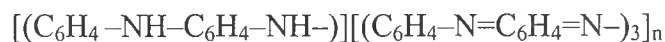
1.2.2 Polyaniline

Polyaniline (PANI) was first made in 1962 by H.Letheby called 'aniline black' (Barici *et al.*, 1996). MacDiarmid *et al.* introduced it as a conductive polymer in 1977 because of its chemical structure (Cao *et al.*, 1989). Polyaniline is attractive because the aniline monomer is inexpensive, good environment stability, ease of synthesis, and high synthetic yield. Polyaniline is the simple 1,4 coupling product of monomeric aniline molecules (Lux, 1994). It can be synthesized by either electrochemically giving a cohesive film, or chemically by an oxidative polymerization of aniline in aqueous acid solution (Huang *et al.*, 1986). Polyaniline has the generalized composition containing a reduced repeating unit and an oxidized repeating unit. The chemical formula of polyaniline can be described as:
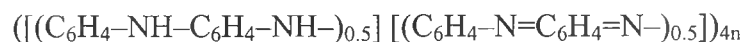
$$([(C_6H_4-NH-C_6H_4-NH-)_{1-x}] [(C_6H_4-N=C_6H_4=N-)_x])_{4n}$$
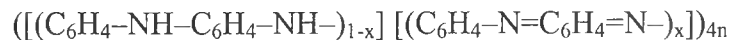
By varying the oxidation level, polyaniline can be converted into 5 different oxidation states (Huang, 1986). The first one is pernigraniline (x=1):

$$(C_6H_4-N=C_6H_4=N-)_{4n}$$
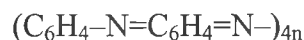
which is of the fully oxidized form having a violet color. The second one is blue-black and called nigraniline:

$$[(C_6H_4-NH-C_6H_4-NH-)][(C_6H_4-N=C_6H_4=N-)_3]_n$$
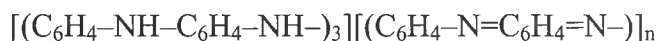
The third one is emeraldine base (x=0.5):

$$([(C_6H_4-NH-C_6H_4-NH-)_{0.5}] [(C_6H_4-N=C_6H_4=N-)_{0.5}])_{4n}$$

which is the general state of polyaniline with a dark blue color consisting of alternating oxidized and reduced repeating units.

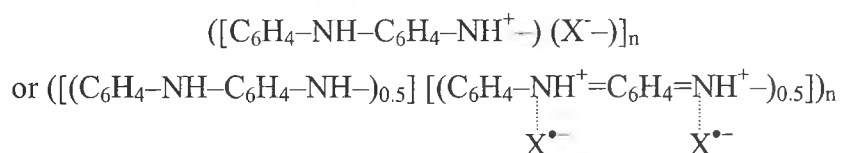Protoemeraldine base is the forth type of polyaniline which has a blue color:

$$[(C_6H_4-NH-C_6H_4-NH-)_3][(C_6H_4-N=C_6H_4=N-)]_n$$

The last one is yellow, a fully reduced form, and is called leucoemeraldine base (x=0):

$$(C_6H_4-NH-C_6H_4-NH-)_{4n}$$
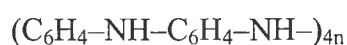
Its color depends strongly on the details of the reaction, for instance, the size of the reaction flask, stirrer speed, and reaction temperature (Lux, 1994).

In general, a polyaniline salt has a green color:

$$([C_6H_4-NH-C_6H_4-NH^+-)\ (X^--)]_n$$
$$\text{or}\ ([(C_6H_4-NH-C_6H_4-NH-)_{0.5}]\ [(C_6H_4-NH^+=C_6H_4=NH^+-)_{0.5}])_n$$
$$X^{\bullet-}\qquad X^{\bullet-}$$

Polyaniline salt is obtained through the doping process that converts an emeraldine base into an emeraldine salt. There are 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, whilst protonation causes no change in the number of π electrons.

1.2.3 Conductive Polymer Sensor

In the case of conductive polymer sensors, electrophilic gases such as NO_2, SO_2 interact with conductive polymers by withdrawing electrons from the chain, thereby increasing the number of charge carriers and hence electronic conductivity. Nucleophilic gases such as NH_3 have the opposite effect resulting in conductivity decrease (Agbor *et al.*, 1995).

Polyaniline, when used as sensor material, has been shown to be able to detect different vapors like methanol, ethanol, acetone, and benzene (Kukla, 1996) and gas sensor such as NH_3 and NO_2 (Li, 2000) and SO_2 (Agbor *et al.*, 1995) at room temperature. In general, current technology does not allow a single specific analyte to be detected. Preliminary studies (Barisci, 1996) on polyaniline sensors reported that the sensor gave a differing magnitude of response, but there was no selectivity for a particular gas. Some selectivity is possible by using an array of sensors and software capable of pattern recognition. A multisensor array coupled to a neutral network has been developed by Barker *et al.*. Other work involving the use of LB has also been used in a unique combination with polypyrrole (PPy); as molecular sieve to improve the sensitivity to alcohol vapours. It needed a clean room and a high temperature process (Barisci, 1996). Conductive polymer composites have become an alternative way to improve the selective gas sensing properties of conductive polymers. While it might be expected that this approach would lead to lower sensitivity, this does not emerge as a significant problem.

1.2.4 Zeolite

Zeolites are naturally and synthetically occurring aluminosilicate minerals with three-dimensional structure based on $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ polyhedra, Their corners link these polyhedra to produce an open structure that has internal cavities in which molecules of various sizes can be trapped. These internal voids, engineered to have specific opening size ranges, trap and hold a variety of molecules that enter the structure matrix, as shown in Scheme 1.1 (Dyer, 1993)
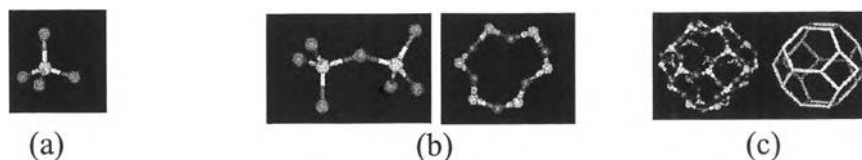
Scheme 1.1 Zeolite structure: (a) $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$, (b) $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ polyhedral, (c) an open structural form.

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 sizes, zeolite plays a very important in the molecular sieving selectivity. At present the large-scale application is in air separation, gas purification and drying agent: for example water treatment, odor control, and industrial gas separation and reinforcement filler (Dyer, 1993). Early works, zeolite was used as template synthesis of polyaniline to produce nanocomposite device (Wu, 1994 and Frish, 1996) and used as an ethanol filtering material, which was coated on the above CO sensing layer to depress such a high sensitivity to C_2H_5OH (Fukui and Nishida, 1997).

The size selectivity and shape selectivity of zeolite crystals to gaseous molecule can be introduced to improve the selectivity and sensitivity of polyaniline sensor. Zeolite A (LTA) has a 3-dimensional pore structure. The pore diameter is defined by an eight-member oxygen ring, which is about 2.3-4.2 Å depending on cation type. This leads into a larger cavity of minimum free diameter 11.4 Å, which is large enough to adsorb CO molecules but on the other hand larger molecules cannot enter. The zeolite A is normally synthesized in the Na^+ form, $Na_{12}Al_{12}Si_{12}O_{48}27H_2O$. In this work, we studied the effect of acid-doped polyaniline and prepared PANI/Zeolite A composites prepared from different zeolite types and contents using dry mixing with the expectation to improve the selectivity of polyaniline gas sensor.

1.3 Objectives

In this study, we studied the electrical conductivity and sensitivity of PANI and PANI/Zeolite A composite as CO sensor. We investigated the effect of dopant type and content on the electrical conductivity and sensitivity of PANI and the effect of zeolite type and content on the electrical conductivity and sensitivity of PANI/Zeolite A composite as CO sensor.