CHAPTER II

LITERATURE SURVEY

2.1 Poly(*p*-phenylene vinlyene) and Doped Poly(*p*-phenylene vinlyene)

Wessling *et al.* (1967) developed the soluble precursor routes to PPV. This process was based upon aqueous solvent synthesis of poly(p-xylylene-a-dialkylsulfonium halides) from α,α'-bis(dialkyl sulfonium salts), followed by thermolytic formation of the final conjugated polymer. The charged sulfonium groups solubilize the polymer and are removed during the conversion step. Molecular weights for the polyelectrolyte are in the 10,000 to.1,000,000 range, which may be precipitated or dialyzed to give typical yields of about 20% high molecular fraction.

Sakamoto *et al.* (1991) studied the resonance Raman spectra of sodium-doped poly(*p*-phenylenevinylene) (PPV) and the radical anions and dianions of three model compounds $CH_3(C_6H_4CH=CH)_nC_6H_4CH_3$ (PVn, n = 1-3). The Raman spectra of sodium-doped PPV show marked changes with laser wavelengths used for Raman excitation. These spectra have been analyzed on the basis of the resonance Raman spectra of the radical anions and dianions of the model compounds, which correspond, respectively,to negative polarons and bipolarons in PPV. Three kinds of negative polarons whose lengths were close to PV1, PV2, andPV3, and a bipolaron which is localized in a region close to PV3, exist in a sodium-doped PPV film. Upon prolonged heat treatment of the sodium-doped PPV (290 °C, 12 h), the shortest polaron corresponding to the radical anion of PVl disappeared, probably because it combined with another polaron to form a bipolaron. These results indicated that resonance Raman spectroscopy is a powerful tool for characterizing polarons and bipolarons in conducting polymers.

Sakamoto *et al.* (1991) observed the resonance Raman and infrared spectra of sulfuric-acid-treated poly(*p*-phenylenevinylene) (PPV) on the basis of the resonance Raman spectra of the radical-cation and dication species of the model compounds $CH_3(C_6H_4CH=CH)_nC_6H_4CH_3$ (PVn, n = 1-3), which corresponded, respectively, to the positive polarons and the bipolarons in PPV. Sulfuric-acid-treated

PPV was considered to contain a considerable amount of positive polarons having a more or less uniform length and a relatively small amount of positive bipolarons. Of the two electronic absorption bands at 2.25 and 1 .OO eV of sulfuric-acid-treated PPV, the former absorption band was due to the positive polarons, whereas the latter had overlapping components arising from the positive polarons and bipolarons. It was suggested that the high electrical conductivity of sulfuric-acid-treated PPV may be due to formation of a polaron lattice, a regular array of polarons.

Massardier *et al.* (1994) used ^{1}H NMR and U.V. spectroscopy to follow the kinetics of p-xylylene tetrahy-drothiophenium dichloride salt polymerization in the presence of sodium hydroxide at 3 and 20°C. The consumption of sodium hydroxide was closely related to the production of sulfide. Reside the polymerization reaction, side reactions were detected which were favored by increasing the reactants concentration as well as the temperature.

2.2 Poly(*p*-phenylene vinlyene) for gas sensor

Babudri *et al.* (2002) developed gas sensors of thin films of a bridged chain dialkoxy PPV derivative bearing a bridged chain dialkoxy substituent on the aromatic rings. Films were prepared via solvent casting and langmuir-Blodgett(LB) techniques. This sensor exhibited the selectivity towards NO_2 with respect to other different gases like CO, NO, NH_3, SO_2. On the contrary, LB multilayers, containing arachidic acid, did not shown any sensitivity toward all target gases.

2.3 Zeolites for gas sensor

Kaneyasu *et al.* (2000) developed a practical CO_2 gas sensor for air quanlity control by using a combination of a $Na_3Zr_2Si_2PO_{12}$ (NACICON) as a solid electrolyte and Li_2CO_3 as a carbonate phase. The sensor's electromotive force showed a linear relation ship with the logalithm of CO_2 concentration. Zeolite was chosen as a filter material in order to minimize the effect of interfering gases on the sensor's emf and shows very little deterioration to CO_2. Under continuous energizing, both the emf and change in emf were stable over a period of 2 years.

Wakita *et al.* (2001) studied the removal of dimethysulfide (DMS) and t-butylmercaptane (TBM) from city gas by using zeolites Na-Y, Na-X and Ca-X. The results showed that high removal ratio of sulfer compounds at 1 h after the adsorption run in city gas flow, though DMS broke though rapidly for a few hours. On the other hand, H-ß and USY showed continuously high removal ratios for 9 h, and trace amounts of HS were detected at the effluent gas. The adsorption mechanisms on Na-Y and H-ß were studied by adsorption in the absence of hydrocarbons which suggested that the adsorption states at binary adsorption were similar to those at single component adsorption. The main adsorption site was presumably Na^+

Sasaki *et al.* (2002) deposited three different zeolites, zeolite A, silicalite-1 and sodalite on the qartz crystal microbalance (QCM) oscillators with fundamental resonance frequency of 4.7MHz. The QCMs with zeolite as reference, were exposed to single gases such as NO, SO_2 and H_2O in He at 433 K. These results suggest that the sensor system with the different values of adsorption kinetics, instead of the frequency shifts representing sorption-equilibria, overcame the disadvantages of the conventional QCM sensors. The system showed favorable qualification and quantification performance for gas mixture.

Giaya and Thompson (2002) characterized the hydropobicity of some microporous materials and obtained adsorption isotherm of some chlorinated volatile organic compounds (CVOCs) by using a tapered element oscillating microbalance. The adsorption of pure component CVOCs showed that DAY sample had higher limiting adsorption capacity than silicalite-1 sample. The opposite behavior was observed when the CVOCs adsorption was in the presence of water. These data supported the conclusion that water interferes with the adsorption of CVOCs in these materials, even though they exhibited significant hydrophobic character.

Despres *et al.* (2003) studied the interaction of NO_X from lean exhaust gases with copper-exchanged ZSM-5 by combined adsorption and temperature-programmed desrption. Experiments with NO at 200 °C showed that this molecule cannot be stored within Cu-ZMS-5. On the other hand, NO_2 may be stored over a wide temperature range from both dry and humid feeds. Therefore, in order to store of NO , NO must first be oxidized to NO_2 . However, the oxidation reaction was exhibited by water in the exhaust gas.

Harlick *et al.* (2004) studied the selection of a suitable adsorbent for CO_2 from flue gas (miture of CO_2 and N_2) with 13 zeolite based adsorbent including 5A, 13X, NaY, NaY-10, H-Y-5, H-Y-30, H-Y-80 , HiSiv 1000, H-ZSM-5-50, H-ZSM-5-80, H-ZSM-5-280, and HiSiv 3000. The CO_2 pure component adsorption isotherms and expected working capacity curves for pressure swing adsorption (PSA) application were determined for a selected promising group of these adsorbents. The results showed that the most promising adsorbent characteristics was a linear CO2 isotherm and a low Sio2/Al2o3 ratio with cations in the zeolite structure which exhibited strong electrostatic interaction with CO_2.

2.4 Conductive polymer/Zeolite for gas sensor

Densakulprasert *et al.* (2005) investigated the effect of zeolite content, pore size and ion exchange capacity on electrical conductivity response to carbon monoxide (CO) of polyaniline/zeolite composites. Zeolite Y, 13X and synthesized AlMCM 41, all having common cation Cu2+, were dry mixed with synthesized maleic acid dope polyaniline and compress to form polyaniline/zeolite composites. The Y, 13X and AlMCM 41 zeolite had the nominal pore sizes of 7, 13 and 36 °A and the Cu2+ capacities of 0.161, 0.087 and 0.044 mol/g,respectively. The highest electrical conductivity sensitivity was obtained with the 13X > Y > AlMCM41. Poor sensitivity of zeolite AlMCM 41 was probably due to its very large pore size and its lowest Cu^{2+} capacity. Zeolite Y and 13X had comparable pore sizes but the latter had a greater free volume and more favorable location distribution of Cu^{2+} ions within the pore. The temporal response time increased with the amount of zeolite in the composites but inversely related to the amount of ion exchange capacity.

Chupradit *et al.* (2005) studied the electrical conductivity response of polyaniline/zeolite composites towards CO in terms of dopant type, dopant concentration, zeolite LTA content and zeolite pore size. Both MA and HCl doped polyanilines responded with comparable magnitudes towards CO; the latter responses were slightly smaller for the same doping level. Addition of zeolite 4A reduced the electrical conductivity response but improved the sensitivity towards CO with increasing concentration up to 40% w/w. This concentration was evidently below the percolation threshold value, which is estimated to be above 50% w/w. Composite with zeolite 3A has comparable sensitivity value relative to that of pure polyaniline. Compoites 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 have the pore size of 4 and 3 Å, respectively.