

CHAPTER III

SENSITIVE AND SELECTIVE RESPONSE OF POLY(PARA-PHENYLENE VINYLENE)/ZEOLITE Y-BASED SENSORS TOWARDS KETONE VAPORS

3.1 Abstract

Poly(p-phenylene vinylene) doped with H_2SO_4 was mixed into zeolite Y matrixed to improve the electrical conductivity responses towards ketone vapors. The effects of cation type, cation concentration, and ketone vapor type on the electrical conductivity response towards ketone vapors of dPPV_zeolite Y composites were investigated. The sensitivities of the composites increased linearly with increasing surface area and cationic radius of the cation in zeolite Y. The highest sensitivity was obtained with the dPPV_ $[90]NH_4^+Y$ when exposed to acetone, whereas in MIBK showed the lowest sensitivity. The interactions between the ketone molecules and the composites were investigated through the FTIR.

Keywords: Conductive Polymer, Gas Sensor, Poly(p-Phenylene Vinylene), Acetone, MEK, MIBK, and Zeolite Y

3.2 Introduction

Semiconductor gas sensors are widely used in domestic and industrial applications due to the favorable characteristics such as low cost and the ease of operation. The sensors still play an important role in the development and the improvement of public health through several aspects (Heeger *et al.*, 1998; Monsteral *et al.*, 2007; Alskas *et al.*, 2011; Luo *et al.*, 2011; Shulka *et al.*, 2011; Vijayakuma *et al.*, 2012). In the color industry, many solvents are utilized to prepare enamel paints: dimethyl ketone or propanone (acetone); methyl ethyl ketone or butan-2-one (MEK); methyl iso-butyl ketone or 4-methylpentan-2-one (MIBK); and 1, 4-dimethylbenzene (p-xylene). These solvents constitute flammable ingredients in the enamel paints, CED and AED paints, car coating paints, and various ingredients used in chemical plants (Mori *et al.*, 2009).

Several conductive polymers have been used as a gas sensing materials: polyaniline (PANi) and polypyrrole (PPy) have many common interesting features such as inexpensiveness, the ease in the syntheses, the high electrical conductivity, and the chemical stability. Another conductive polymer, poly(p-phenylene vinylene) or PPV is also a candidate. It has good mechanical properties, the high electrical conductivity, as well as the chemical stability. PPV can be synthesized to yield a high molecular weight polymer. In the first step, the formation of the precursor is *via* the Wessling route, followed by the synthesis of the polymer from such precursor *via* the thermal reaction. Recently, PPV and their oligomers have been shown to be useful as active materials for gas sensors or for electronic noses (Peres *et al.*, 2007; Das *et al.*, 2012).

Zeolites are polycrystalline, hydrated aluminosilicates of Group I and Group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium. Structurally, the zeolites are “framework” aluminosilicates which are based on an infinitely extending three-dimensional network of $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ tetrahedral linked to each other by sharing all of the oxygen. The framework contains channels and interconnected voids which are occupied by the cations and water molecules. The cations are quite mobile and may be easily exchanged by other cations. Because of their unique structure, zeolites and related microporous materials possess the molecular sieving property which is useful as catalysts, adsorbents, and in the ion exchanging. As a sensing material, zeolites are very advantageous: high thermal stability and chemical resistance. Characteristics of the molecular sieving property have been explored and utilized as chemical sensors (Mori *et al.*, 2009; Yang *et al.*, 2007). Recently, composites consisting of the zeolite that is dispersed in a polymer matrix have been investigated as sensing materials to detect toxic gases (Yang *et al.*, 2007; Mishira *et al.*, 2011; Shama *et al.*, 2012).

Combining the advantages of the two materials, we propose to investigate the combination of a conductive polymer, PPV, and zeolite Y of various cations as ketone vapor sensors. The effects of dPPV concentration, cation type of zeolite Y, and the ketone solvent type on the electrical conductivity response of the composites will be investigated and reported here.

3.3 Experimental

3.3.1 Materials Preparation

3.3.1.1 *Synthesis of Poly(p-Phenylene Vinylene) or PPV*

The synthesis of the p-xylene-bis(tetrahydrothiophenium chloride) monomer was achieved by reacting α,α' -dichloro-p-xylene (Aldrich) with tetrahydrothiophene (Aldrich) (Wessling *et al.*, 1968). The precursor poly(p-xylene-bis(tetrahydrothiophenium chloride) or precursor PPV was prepared in an aqueous solution by the sodium hydroxide induced polymerization of an appropriate p-xylene-bis(tetrahydrothiophenium chloride) monomer. The polymerization reaction was terminated by the addition of dilute aqueous hydrochloric acid to the reaction mixture which was then dialyzed against water in order to separate the high molecular weight fraction from the monomeric and oligomeric residues as well as the sodium and chloride ions. PPV was essentially obtained by heating precursor PPV under vacuum at 180 °C for 6 h (Wessling *et al.*, 1968; Peres *et al.*, 2007).

3.3.1.2 *Doping Process*

The 18 M sulfuric acid was used as the dopant solution at the mole ratio between PPV repeating unit per sulfuric acid equal to 1:100. The doping process occurred after adding the dopant solution to the polymeric powder, and it was monitored by observing the color changes of the powder from bright yellow to black (Ahlskog *et al.*, 1997).

3.3.1.3 *Preparation of dPPV_Zeolite Y Pellet*

Zeolite: CBV100 (Si/Al=5.1 and Na⁺) (Zeolyst) or NaY, CVB300 (Si/Al=5.1 and NH₄⁺) (Zeolyst) or NH₄⁺Y, and CVB 400 (Si/Al=5.1 and H⁺) (Zeolyst) or HY were used as the adsorbents. dPPV_zeolite Y composites were prepared by dry mixing the doped PPV particles with the zeolite Y at 10% v/v. The composites were compressed into a disc form by using a hydraulic press at the pressure of 6 kN.

3.3.2 Materials Characterization

The FT-IR spectrometer (Bruker, model FRA 106/S) was used to characterize functional groups of PPV and the interaction between the chemical vapors and the composites. A scanning electron microscope (SEM, Hitachi, model S4800) was used to study the morphology of PPV, doped PPV or dPPV, the zeolite Y, and the 10% v/v of dPPV_zeolite Y composites and the dispersion between the conductive polymer and the zeolite Y at the magnifications of 2000 and 5000 and at 5 and 10 kV. BET (Sorptomatic-1990) was used to measure the pore sizes and the surface areas of the zeolite Y. A custom made two-point probe with a linear geometric array was used to measure the specific electrical conductivity of samples.

3.3.3 Electrical Conductivity and Chemical Vapor Detection

The electrical conductivity of the PPV pellets under exposures to air, N₂, and chemical vapors were measured by using the custom made two-point probe, in the chemical chamber, connected to a voltage supplier (Keithley, 6517A) in which its voltage was varied and the resultant current was measured. The electrical conductivity was calculated by utilizing the equation: $\sigma = (I/KVt)$; where I is the measured current (A); V is the applied voltage (V); t is the thickness; and K is the geometric correction factor of the two-point probe determined by calibrating the probe with a silicon wafer possessing a known resistivity value. The chemicals used in this work were dimethyl ketone or propanone (acetone), methyl ethyl ketone or butan-2-one (MEK), and methyl iso-buthyl ketone or 4-methylpentan-2-one (MIBK) (labscan, AR grade). All of ketone vapors were prepared through a flow system at the vapor concentration of 30000 ppm. Nitrogen (N₂, TIG) was used as the surface cleaning gas and to vaporize the chemical solvents. All chemicals were used without further purifications. The electrical conductivity response and sensitivity of the composites were determined by following the equations: $\Delta\sigma = \sigma_{\text{chemical vapor}} - \sigma_{\text{N}_2, \text{ before exposure}}$ and $\Delta\sigma / \sigma_{\text{N}_2, \text{ before exposure}}$, respectively. $\Delta\sigma$ is the difference in the specific electrical conductivity (S/cm), $\sigma_{\text{N}_2, \text{ before exposure}}$ is the specific electrical conductivity in N₂ before exposure (S/cm), and $\sigma_{\text{chemical vapor}}$ is the specific electrical conductivity

under chemical vapor exposure (S/cm) (Chuapradit *et al.*, 2005; Densakulprasert *et al.*, 2005; Thuwachaosoan *et al.*, 2007).

3.4 Results and Discussion

3.4.1 Morphology of DPPV Zeolite Y

Figure 3.1 shows the SEM monographs of dPPV or doped poly(p-phenylene vinylene), zeolite Y (Si/Al=5.1 and NH_4^+) or NH_4^+Y , and dPPV_zeolite Y (Si/Al=5.1 and NH_4^+) or the dPPV_[90] NH_4^+Y composite at the dPPV volume fraction of 10% v/v. The dPPV particles are quite irregular in shape and size, as shown in Figure 3.1a. On the other hand, the zeolite Y appears to possess nearly uniform sizes and shapes, as shown in Figure 3.1b. However, a nearly uniform dispersion of dPPV particles within the NH_4^+Y matrix can be observed in Figure 3.1c and 3.1d (Thuwachaosoan *et al.*, 2007).

3.4.2 Temporal Response of Zeolite Y and Composites when Exposed to Ketone Vapors

The temporal response of the composites is investigated next. The induction time is defined as the time required for the electrical conductivity to reach the equilibrium value when exposed to chemical vapors. The recovery time is defined as the time required for the electrical conductivity to attain the equilibrium value when chemical vapors are removed and replaced with nitrogen (Thuwachaosoan *et al.*, 2007). Table 3.1 lists the induction times and the recovery times of the zeolite Y and the composites. The induction times of NH_4^+Y , NaY, and HY when exposed to acetone vapor at concentration of 30000 ppm in N_2 are 44 ± 1 , 42 ± 2 , and 29 ± 6 min, respectively. The recovery times of these samples are 15 ± 5 , 27 ± 2 , and 20 ± 2 min, respectively. The induction time of NH_4^+Y is the longest. This number is directly related to the specific surface area and the number of active sites in the zeolite Y framework. NH_4^+Y has the highest specific surface area ($766 \pm 3 \text{ m}^2/\text{g}$), whereas the NaY and HY surface areas are $731 \pm 12 \text{ m}^2/\text{g}$ and $648 \pm 2 \text{ m}^2/\text{g}$; thus the acetone vapor can penetrate more easily into the NH_4^+Y structure and take the longer time than those of NaY and HY (Panov *et al.*, 1998). The recovery time of

NaY is longer than HY because Na^+ has the higher surface area than H^+ , thus NaY is more interaction sites with acetone vapor and take the longer time than HY (Panov *et al.*, 1998; Thuwachaosoan *et al.*, 2007). On the other hand, the recovery time of NH_4^+Y is 15 ± 5 min, the shortest, is due to the fact that NH_4^+ is not main elements and thus interacts weakly with the acetone vapor. For the other ketone vapors (MEK and MIBK); the results are similar. We may note that the induction times of NH_4^+Y when exposed to acetone, MEK and MIBK are 44 ± 1 , 30 ± 2 , and 22 ± 2 min, respectively; these values are higher than those NaY and HY due to the highest surface area of NH_4^+Y . The corresponding recovery times are 15 ± 5 , 13 ± 1 , and 12 ± 1 min, respectively; these values are lower than those NaY and HY due to the highest surface area of NH_4^+Y . These numbers can also directly relate to the number of available active sites for the ketone vapor molecules. Since the size of acetone molecule is smaller than those of MEK and MIBK, it can penetrate further into the zeolite to interact with the available active sites and take the longer times than those of MEK and MIBK (Panov *et al.*, 1998; Ruangchuay *et al.*, 2003). Adding 10% v/v of dPPV into NH_4^+Y matrix and exposing it to acetone, MEK, and MIBK vapors at the concentration of 30000 ppm in N_2 , the induction times of composites decrease to 31 ± 3 , 21 ± 1 , and 11 ± 2 min, respectively. The presence of dPPV reduces the available active sites on the zeolites Y, surface area and therefore the time to reach equilibrium is shorter. For other cations (Na^+ and H^+) in the composites, similar results are obtained as the dPPV_[90] NH_4^+Y composite with respect to the ketone vapors (Ruangchuay *et al.*, 2003; Thuwachaosoan *et al.*, 2007). In a previous work, the response time of the PS/PMMA/ABS blend to acetone vapor was shorter relative to those of the individual polymers (Ruangchuay *et al.*, 2003).

3.4.3 Electrical Conductivity Sensitivity of Zeolite Y and DPPV Zeolite Y when Exposed to Ketone Vapors

Doped poly(p-phenylene vinylene) is mixed with NH_4^+Y at various dPPV contents: 0; 10; 20; 40; 60; 80; and 100% v/v. Figure 3.2 shows the electrical sensitivity of dPPV_ NH_4^+Y when exposed to acetone vapor at the concentration of 30000 ppm in N_2 . The electrical sensitivity of the composites with the dPPV contents between 0 to 40% v/v increases from $4.32 \times 10^{-01} \pm 1.30 \times 10^{-02}$ to $4.13 \pm 5.55 \times 10^{-02}$,

an increase by nearly an orders of magnitude. For the dPPV contents between 60 to 80% v/v, the electrical conductivity sensitivity decreases from $3.84 \pm 2.89 \times 10^{-02}$ to $3.77 \pm 7.09 \times 10^{-03}$. The initial increase in the electrical conductivity sensitivity between 0% v/v to 40% v/v of dPPV is due to the higher sensitivity of dPPV to acetone relative to that of NH_4^+Y , $4.49 \pm 6.78 \times 10^{-01}$ vs $4.32 \times 10^{-01} \pm 1.30 \times 10^{-02}$, a difference by an order of magnitude, as shown in Table 3.1. The decrease in the electrical conductivity sensitivity at the high content of dPPV is due to the reduced amount of the porous zeolite which promotes the vapor molecules to interact with the available active sites of dPPV (Chuapradit *et al.*, 2005; Densakulprasert *et al.*, 2005; Thewachaosoan *et al.*, 2007; Panov *et al.*, 1998). From this result, the composite with the 10% v/v of dPPV content is then chosen for further study on the electrical conductivity responses towards other ketone vapors since the sensitivity of the composite at 10% v/v of dPPV gives the sensitivity quite close to that of the pristine dPPV (Chuapradit *et al.*, 2005; Densakulprasert *et al.*, 2005; Thewachaosoan *et al.*, 2007; Ruangchuay *et al.*, 2003) as shown in Table 3.1.

The effect of cation type of the zeolite Y and the composites on the responses to the acetone vapor is investigated next. Table 3.1 lists the electrical conductivity responses and the sensitivity values of the zeolite Y and the composites of various cations. The electrical conductivity sensitivity values of zeolite Y with the cations of NH_4^+ , Na^+ , and H^+ when exposed to acetone vapor at the concentration of 30000 ppm are $4.32 \times 10^{-01} \pm 1.30 \times 10^{-02}$, $2.68 \times 10^{-01} \pm 1.99 \times 10^{-02}$, and $1.52 \times 10^{-01} \pm 2.48 \times 10^{-02}$, respectively. Thus, NH_4^+Y possesses the highest sensitivity. Typically, the gas adsorption properties and the interactions are expected to depend on 3 factors: the specific surface area, the electronegativity value (EN), and the ionic radius (Å) The specific surface areas of zeolite Y with the cations of NH_4^+ , Na^+ , and H^+ are 766 ± 3 , 731 ± 12 , and $648 \pm 2 \text{ m}^2/\text{g}$, respectively. NH_4^+Y have the highest specific surface area facilitating a larger amount of acetone vapor into the zeolite framework. In case of the cationic radii, NH_4^+ (1.75 Å) is larger than Na^+ (1.16 Å) and H^+ (0.37 Å) which reduced the electrostatic interaction with the anionic zeolite framework and cation which lead to the ease of interaction between cation in the zeolite Y framework and acetone (Yimlamai *et al.*, 2011). For the 10% v/v of dPPV_zeolite Y composites with the three types of cation (NH_4^+ , Na^+ , and H^+), the

sensitivity values to acetone increase to $3.82 \pm 3.12 \times 10^{-02}$, $2.09 \pm 5.26 \times 10^{-02}$, and $1.30 \pm 8.22 \times 10^{-02}$, respectively. These values are higher than those of the pristine zeolites Y by an order of magnitude, due to the presence of dPPV. The higher sensitivity values of the dPPV_zeolite Y composites than those of the pure zeolite Y is due to the available active sites along the dPPV chains. The positive increments in the sensitivity upon exposed to all of the ketone vapors imply that the solvent molecules act as a primary and a secondary dopant for PPV or doped PPV, resulting in a greater number of charges along the polymer backbone and correspondingly a larger sensitivity (Kamonsawas *et al.*, 2010) as shown in Figure 3.3 and Table 3.1.

The effect of ketone vapor type on the electrical conductivity sensitivity is investigated next. The electrical conductivity sensitivity values of NH_4^+Y when exposed to acetone, MEK, and MIBK at the vapor concentration of 30000 ppm in N_2 are $4.32 \times 10^{-01} \pm 1.30 \times 10^{-02}$, $3.68 \times 10^{-01} \pm 3.23 \times 10^{-02}$, and $2.14 \times 10^{-01} \pm 3.50 \times 10^{-01}$, respectively, as shown in Table 3.1. These values are comparable in magnitude, and similar results are obtained for NaY and HY. On the other hand, for the dPPV_ [90] NH_4^+Y composites, the sensitivity values are $3.82 \pm 3.12 \times 10^{-02}$, $2.76 \pm 1.80 \times 10^{-01}$, and $1.02 \pm 3.58 \times 10^{-01}$, respectively. The molecular sizes are 5.246, 6.667, and 8.286 Å for acetone, MEK, and MIBK, respectively. The smaller size of the ketone vapor molecule leads to a better interaction between the vapor and the active sites (Panov *et al.*, 1998; Ruangchuay *et al.*, 2003; Soontornworajit *et al.* 2007; Kamonsawas *et al.*, 2010; Yimlamai *et al.*, 2011).

3.4.4 FTIR Investigations of Reactions of Adsorbed Ketone Vapor

The FTIR spectra of NH_4^+Y and dPPV_ [90] NH_4^+Y were taken in the 650-4000 cm^{-1} regions (Figures 3.4 and 3.6). The spectra are for before (a), during 15 minutes interval (b), and after the acetone exposure (c) in order to study the interaction between the zeolite Y and acetone.

Figure 3.4 shows the FTIR spectra of NH_4^+Y before (a), during 15 minutes interval (b), and after the acetone exposure (c). Before the acetone exposure, the adsorption of the Si-OH group ($\nu = 3640 \text{ cm}^{-1}$) can be assigned to the zeolite characteristic (Gaare *et al.*, 1997; Panov *et al.*, 1998; Hagen *et al.*, 2006; Soontornworajit *et al.*, 2007; Li *et al.*, 2010; Yimlamai *et al.*, 2011). The peaks at

790 and 1010 cm^{-1} are the characteristic of tetrahedral unit (Soontornworajit *et al.*, 2007). The peaks at 1400 cm^{-1} are the stretching and bending of N-H bond in N_2 condition before acetone exposure (Soontornworajit *et al.*, 2007; Yimlamai *et al.*, 2011). A peak at 1600 cm^{-1} is the OH stretching which suggests the possibility of the water in zeolite structure (Panov *et al.*, 1998; Yimlamai *et al.*, 2011). During the acetone exposure, the spectrum shows three new peaks at 3449, 1734, and 1213 cm^{-1} , the former can be assigned to the interaction between oxygen on the carbonyl group and cation into zeolite framework, as shown in Figure 3.5. The new peak at 3449 cm^{-1} is assigned to the interaction between oxygen on the carbonyl group and hydrogen at the zeolite (Gaare *et al.*, 1997; Hagen *et al.*, 2006; Soontornworajit *et al.*, 2007; Li *et al.*, 2008; Kamonsawas *et al.*, 2010; Li *et al.*, 2010; Yimlamai *et al.*, 2011). When acetone is removed and replaced with nitrogen, the IR spectrum peaks at 3449 and 1213 cm^{-1} evidently decrease; this confirms that there are some interactions remaining between acetone and the zeolite, suggesting the irreversible response to acetone (Thuwachaosoan *et al.*, 2007).

Figure 3.6 shows the corresponding IR spectra of dPPV_[90] NH_4^+Y . Before the acetone exposure, the adsorption peak of the quinoid structure, a characteristic of dPPV, appears at $\nu = 1141 \text{ cm}^{-1}$. The peaks at 1514, 2963, and 3017 cm^{-1} are the characteristics of phenylene (Gagnon *et al.*, 1987; Cirpan *et al.*, 2003). The peak at around 3656 cm^{-1} can be assigned to the Si-OH group (Soontornworajit *et al.*, 2007). During the acetone exposure, the two new peaks at 3449 and 1250 cm^{-1} are the interaction between acetone and the zeolite (Gaare *et al.*, 1997; Hagen *et al.*, 2006; Soontornworajit *et al.*, 2007; Li *et al.*, 2010). The new peak at 1377 cm^{-1} indicates the C-O stretching; this also suggests an interaction between acetone and dPPV. The increase in the intensity at 1141 cm^{-1} during the exposure is caused by the increase in number of the quinoid structures of dPPV (Gagnon *et al.*, 1987; Cirpan *et al.*, 2003). After the acetone exposure, the intensities at 3017, 2963, and 1514 cm^{-1} decrease; these suggest that acetone may act as a secondary dopant to increase the number of the quinoid structures and the interactions still remain along the dPPV chain (Kamonsawas *et al.*, 2010; Gagnon *et al.*, 1987; Cirpan *et al.*, 2003). The interaction between acetone with dPPV_[90] NH_4^+Y is proposed and shown in Figure 3.7. The interaction is clearly irreversible.

3.5 Conclusions

Zeolites Y with the three types of cation: NH_4^+ ; Na^+ ; and H^+ was investigated and utilized as ketone vapors sensing materials. Electrical conductivity sensitivity of the zeolites towards ketone could be improved by introducing doped PPV into the zeolite Y matrices. The electrical conductivity sensitivity of zeolite Y and composites increased with increasing zeolite Y surface area and decreasing chemical vapor size. The electrical conductivity sensitivity of dPPV_[90] NH_4^+ Y when exposed to acetone exhibited the highest value at $3.82 \pm 3.12 \times 10^{-02}$ since dPPV_[90] NH_4^+ Y had the highest specific surface area and it could induce the more favorable acetone vapor adsorption in to the composite. The interaction was further investigated by the IR spectra and appeared to be irreversible.

3.6 Acknowledgements

The author would like to acknowledge the financial support from: The Conductive and Electroactive Polymers Research Unit of Chulalongkorn University; The Thailand Research Fund (TRF-RTA, TRF-RGJ PHD0026/2553); The Royal Thai Government.

3.7 References

- Ahlskog, M., Reghu, M., Noguchi, T., and Ohnishi, T. (1997) Doping and conductivity studies poly(p-phenylene vinylene). Synthetic Metals, 89, 11-15.
- Alkskas, I.A., and Moosa, I.S. (2011) Synthesis, characterization, and electrical properties of new crosslinked conjugated polymer based on acetyl acetone moiety. International Journal of Polymeric Materials and Polymeric Biomaterials. 61, 1142-1153.
- Chuapradit, C., Wannatong, L., Chotpattananont, D., Hiamtup, P., Sirivat, A., and Schwank, J. (2005) Polyaniline/zeolite LTA composites and electrical conductivity response towards CO. Polymér, 46, 947-953.

- Cirpan, A., Kucukyavuz, Z., and Kucukyavuz, S. (2003) Synthesis, characterization, and electrical conductivity of poly(paraphenylene vinylene). Turkish Journal of Chemistry, 27, 135-144.
- Das, T.K., and Prusty, S. (2012) Review on conducting polymer and their application. Polymer-Plastics Technology and Engineering, 51, 1487-1500.
- Densakulprasert, N., Wannatong, L., Chotpattananont, D., Hiamtup, P., Sirivat, A., and Schwank, J. (2005) Electrical conductivity of polyaniline/zeolite composites and synergetic interaction with CO. Materials Science and Engineering: B, 117, 276-282.
- Gaare, K. and Akporiaye, D. (1997) Effects of La exchange on NaY and NaX zeolites as characterized by ^{29}Si NMR. Journal of Physical Chemistry B, 101, 48-54.
- Gagnon, D., Capiston, J., Karasz, F.E., and Lenz, R.W. (1987) Synthesis, doping, and electrical conductivity of high molecular weight poly(p-phenylene vinylene). Polymer, 28, 567-573.
- Hagen, G., Dubbe, A., Rettig, F., Jerger, A., Birkhofer, Th., Muller, R., Polg, C., and Moos, R. (2006) Selective impedance based gas sensors for hydrocarbons using ZSM-5 zeolite films with chromium(III)oxide interface. Sensors and Actuators B: Chemical, 119, 441-448.
- Heeger, A.J. and Diaz-Gracia, M.A. (1998) Semiconducting polymers as a material for photonic device. Current Opinion in Solid State Materials Science, 3, 16-22.
- Kamonsawas, J., Sirivat, A., Niamlang, S., Hormnirun, P., and Prissanaroon-Ouijai, W. (2010) Electrical conductivity response of poly(phenylene vinylene)/zeolite composites exposed to ammonium nitrate. Sensors, 10, 5590-5603.
- Li, R.C.W., Ventura, L., Gruber, J., Kawano, Y., and Carvalho, L.R.F. (2008) A selective conductive polymer-based sensor for volatile halogenated organic compound (VHOC). Sensors and Actuators B: Chemical, 131, 646-651.
- Li, X. and Dutta, P.K. (2010) Interaction of dimethylmethylphosphate with zeolite Y: impedance based sensor for detecting nerve agent stimulants. Journal of Physical Chemistry C, 114, 7986-7994.

- Luo, Y.L., Miao, Y., Xu, F., and Yao, Y. (2012) Novel HTPB/MWNT-COOH PU conductive polymer composite films for detection of hazardous organic solvent vapors. Polymer-Plastics Technology and Engineering, 51, 290-297.
- Luo, Y., Yu, W., and Xu, F. (2011) Surface modification and vapor-induced response of poly(vinylidene fluoride)/carbon black composite conductive thin films. Polymer-Plastics Technology and Engineering, 50, 1084-1090.
- Mishra, I., Akinyeye, R., Baker, P., and Iwuoha, E. (2011) Synthesis and characterization of sulfonated polyanilines and application in construction of a diazinon biosensor. International Journal of Polymeric Materials and Polymeric Biomaterials, 60, 469-489.
- Montserral, V., Joaquin, C., Albert, C., Albert, C., Ramon, M.J., and Jesus, S. (2007) Gas detection with SnO₂ sensors modified by zeolite films. Sensors and Actuators B: Chemical, 124, 99-110.
- Mori, M., Nishimura, H., Itagaki, Y., and Sadaoka, Y. (2009) Potentiometric VOC detection in air using 8YSZ-based oxygen sensor modified with SmFeO₃ catalytic layer. Sensors and Actuators B: Chemical, 142, 141-146.
- Panov, A.G. and Fripiat, J.J. (1998) An infrared study of acetone and mesityl oxide adsorption on acid catalyst. Langmuir, 14, 3788-3796.
- Peres, O.P., Fernandes, M.R., Garcia, J.R., Wang, S.H., and Nart, F.C. (2006) Synthesis and characterization of chloro and bromo substituted p-phenylene vinylene homopolymers and alternating copolymers. Synthetic Metals, 156, 529-536.
- Ruangchuay, L., Sirivat, A., and Schwank, J. (2003) Polypyrrole/poly(methyl methacrylate) blend as selective sensor for acetone in lacquer. Talanta, 60, 25-30.
- Ruangchuay, L., Sirivat, A., and Schwank, J. (2004) Electrical conductivity response of polypyrrole to acetone vapor: effect of dopant anions and interaction mechanisms. Synthetic Metals, 140, 15-21.
- Sharma, A.L., Kumar, P., and Deep, P. (2012) Highly sensitive glucose sensing with multi-walled carbon nanotubes-polyaniline composite. Polymer-Plastics Technology and Engineering, 51, 1382-1387.

- Shukl, P., Bhatia, V., Gaur, V., and Jain, V.K. (2011) Electrostatically functionalized multiwalled carbon nanotube/PMMA composite thin films for organic vapor detection. Polymer-Plastics Technology and Engineering, 50, 1179-1184.
- Soontornworajit, B., Wannatong, L., Hiamtup, P., Niamlang, S., Chotpattananont, D., Sirivat, A., and Schwank, J. (2007) Induced interaction between polypyrrole and SO₂ via molecularsieve 13X. Materials Science and Engineering: B, 15, 78-86.
- Thuwachaosoan, K., Chottananont, D., Sirivat, A., Rujiravanit, R., and Schwank, J.W. (2007) Electrical conductivity responses and interactions of poly(3-thiopheneacetic acid)/zeolites L, mordenite, beta, and H₂. Materials Science and Engineering: B, 140, 23-30.
- Vijayakumar, N., Subramanian, E., and Padiyan, D.P. (2012) Conducting polyaniline blends with the soft template poly(vinyl pyrrolidone) and their chemosensor application. International Journal of Polymeric Materials and Polymeric Biomaterials, 61, 847-863.
- Wessling, R.A., and Zimmerman, R.G. (1968) Polyelectrolytes from bis-sulfonium salts. U.S. Patent, 3, 401.
- Yimlamai, I., Niamlang, S., Chanthaanont, P., Kunanuruksapong, R., Changkhamchom, S., and Sirivat, A. (2011) Electrical conductivity response and sensitivity of ZSM-5, Y, and mordenite zeolite towards ethanol vapor. Ionics, 17, 607-615.

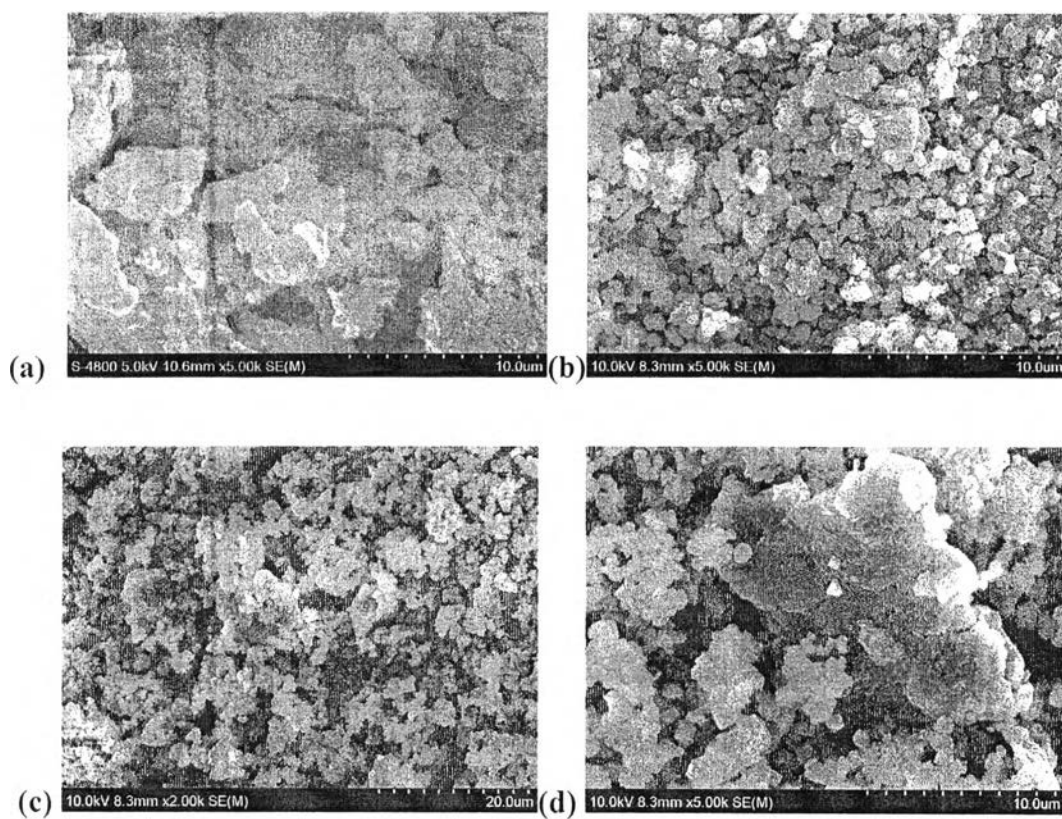


Figure 3.1 The morphology of dPPV, NH_4^+Y powders, and dPPV_90 NH_4^+Y composites at 10% v/v of dPPV: (a) dPPV at magnification of 5000; (b) zeolite Y at magnification 5000; (c) dPPV_90 NH_4^+Y at magnification of 2000; and (d) dPPV_90 NH_4^+Y at magnification of 5000.

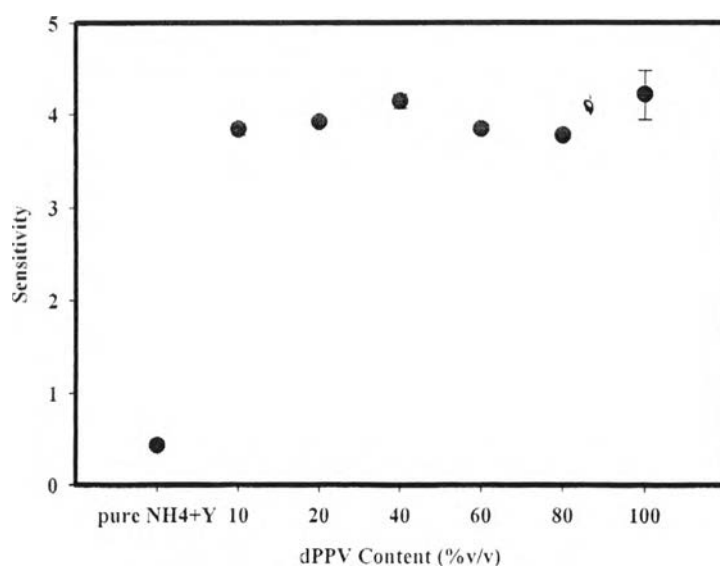


Figure 3.2 Sensitivity of dPPV mixed with zeolite Y (Si/Al=5.1 and NH_4^+) or NH_4^+ Y at various contents: 0; 10; 20; 40; 60; 80; and 100% v/v when exposed to acetone vapor concentration of 30000 ppm in N_2 (at 25 °C and 1 atm).

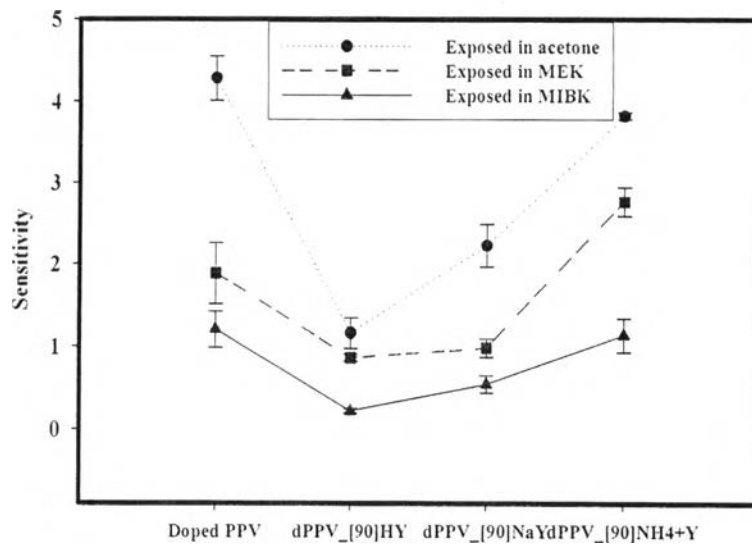


Figure 3.3 Sensitivity values of dPPV, dPPV_[90]HY, dPPV_[90]NaY, and dPPV_[90]NH $_4^+$ Y, when exposed to acetone, MEK, and MIBK at 25 °C, 1 atm, and at the solvent concentration of 30000 ppm in N_2 .

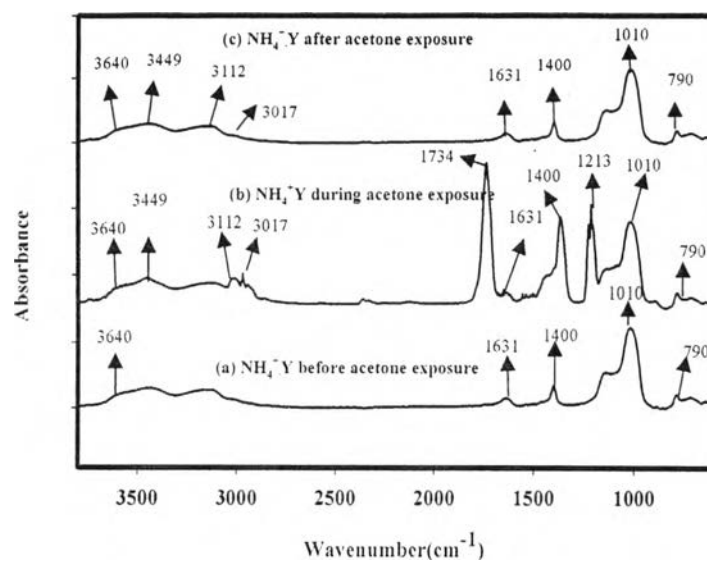


Figure 3.4 FTIR Interaction between NH_4^+Y and acetone at 25 °C, 1 atm before, during, and after the exposure to acetone vapor at the concentration of 30000 ppm in N_2 .

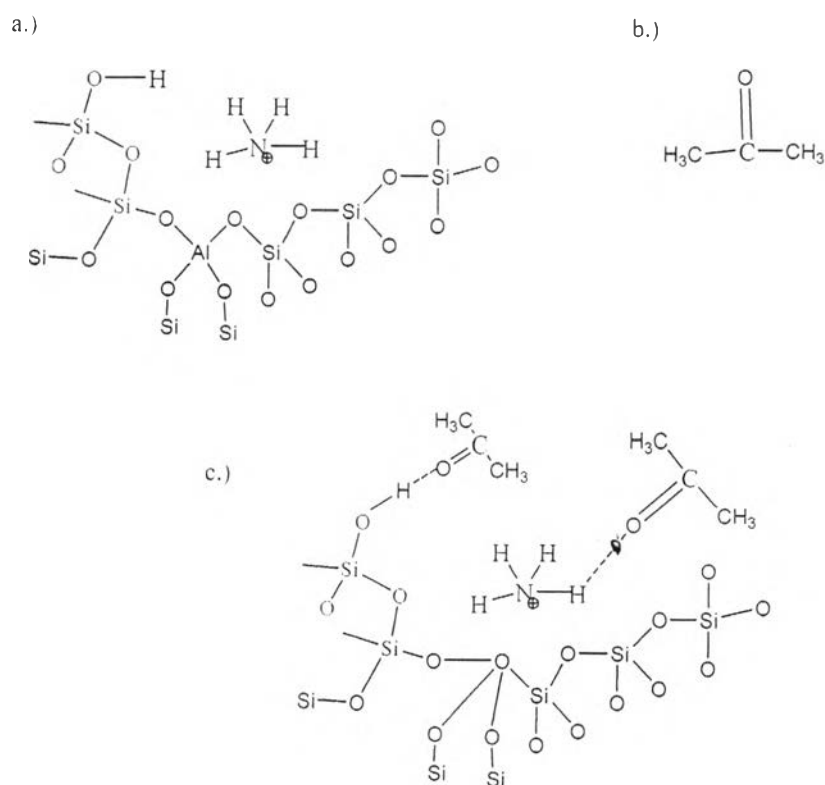


Figure 3.5 Schematic of the proposed mechanism of the acetone-zeolite Y.

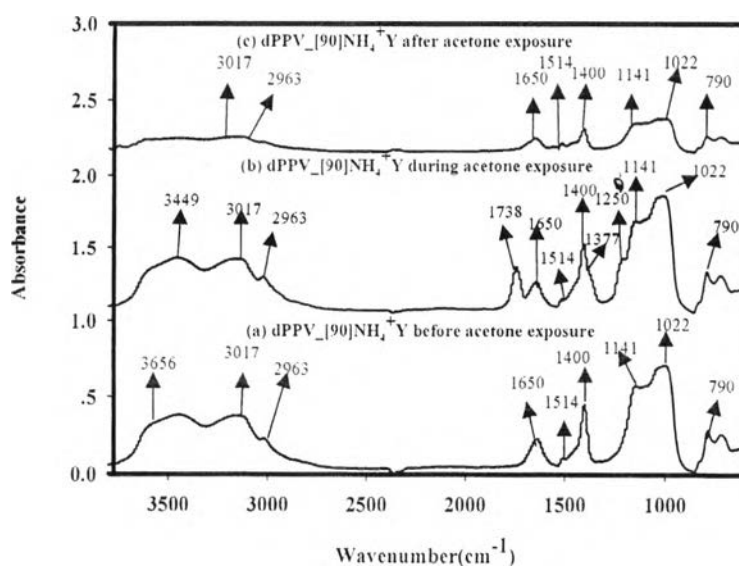


Figure 3.6 FTIR Interaction between dPPV_[90]NH₄⁺Y and acetone at 25 °C, 1 atm before, during, and after the exposure to acetone vapor at the concentration of 30000 ppm in N₂.

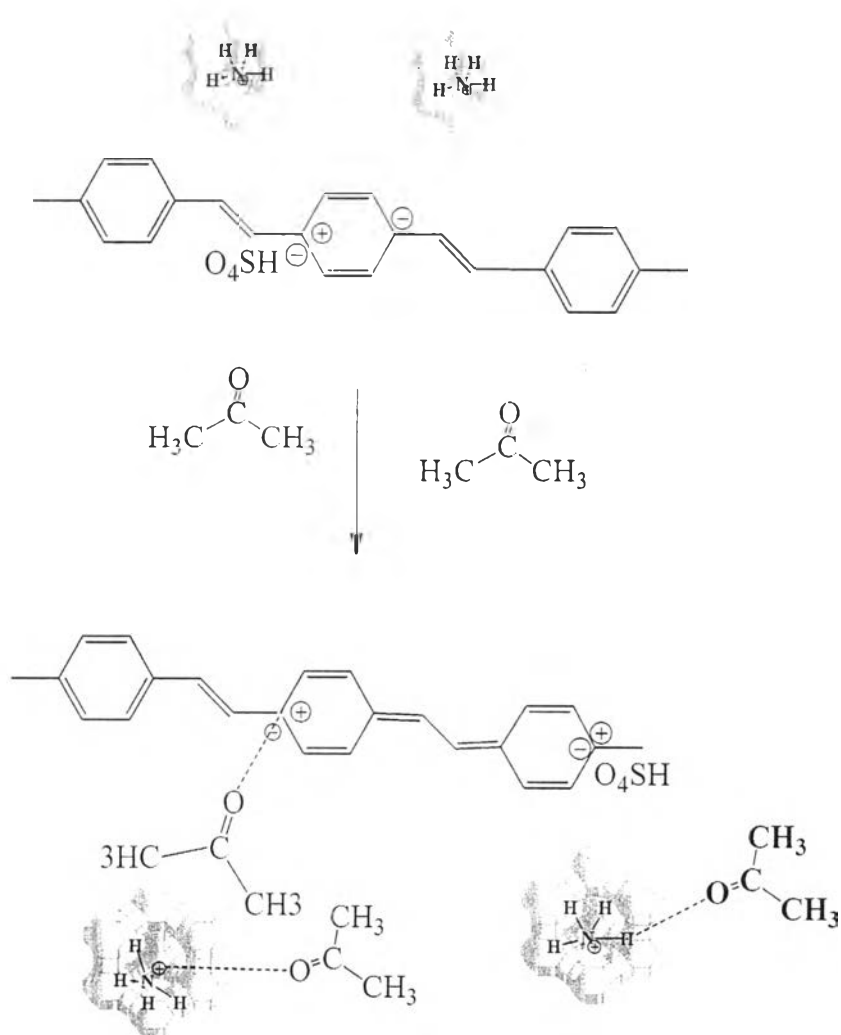


Figure 3.7 Schematic of the proposed mechanism of the acetone-dPPV_[90]NH₄⁺Y.

Table 3.1 PPV, dPPV, and dPPV_zeolite Y composites with the electrical conductivity responses, sensitivities, and temporal responses to acetone, MEK, and MIBK (25 °C, 1 atm, and the vapor concentration of 30000 ppm in N₂) and the specific surface areas.

Sample	Sample Code	BET Surface Area (m ² /g)	Sensitivity			Acetone		MEK		MIBK	
			Acetone	MEK	MIBK	Induction Time (min)	Recovery Time (min)	Induction Time (min)	Recovery Time (min)	Induction Time (min)	Recovery Time (min)
PPV	PPV	-	1.61 x10 ⁻⁰¹ ± 5.08 x10 ⁻⁰²	2.22 x10 ⁻⁰² ± 8.50 x10 ⁻⁰³	1.33 x10 ⁻⁰² ± 1.79 x10 ⁻⁰³	51 ± 2	12 ± 1	19 ± 1	6 ± 3	17 ± 5	8 ± 1
100dPPV	dPPV	-	4.49 ± 6.78 x10 ⁻⁰¹	1.89 ± 3.73 x10 ⁻⁰¹	1.20 ± 2.19 x10 ⁻⁰¹	35 ± 0.2	20 ± 1	32 ± 2	11 ± 5	12 ± 1	10 ± 4
Zeolite Y (Si/Al=5.1 and Na ⁺)	NaY	731 ± 12	2.68 x10 ⁻⁰¹ ± 1.99 x10 ⁻⁰²	1.55 x10 ⁻⁰¹ ± 4.76 x10 ⁻⁰²	1.47 x10 ⁻⁰¹ ± 6.48 x10 ⁻⁰²	42 ± 2	27 ± 2	19 ± 1	20 ± 3	17 ± 4	16 ± 3
Zeolite Y (Si/Al=5.1 and NH ₄ ⁺)	NH ₄ ⁺ Y	766 ± 3	4.32 x10 ⁻⁰¹ ± 1.30 x10 ⁻⁰²	3.68 x10 ⁻⁰¹ ± 3.23 x10 ⁻⁰²	2.14 x10 ⁻⁰¹ ± 3.50 x10 ⁻⁰¹	44 ± 1	15 ± 5	30 ± 2	13 ± 1	22 ± 2	12 ± 1
Zeolite Y (Si/Al=5.1 and H ⁺)	HY	648 ± 2	1.52 x10 ⁻⁰¹ ± 2.48 x10 ⁻⁰²	7.94 x10 ⁻⁰² ± 6.59 x10 ⁻⁰³	4.01 x10 ⁻⁰¹ ± 1.00 x10 ⁻⁰³	29 ± 6	20 ± 2	17 ± 1	15 ± 4	16 ± 6	13 ± 1
DPPV_[90]zeolite Y (Si/Al=5.1 and Na ⁺)	dPPV_[90]NaY		2.09 ± 5.26 x10 ⁻⁰²	9.38 x10 ⁻⁰¹ ± 1.51 x10 ⁻⁰¹	5.43 x10 ⁻⁰¹ ± 1.07 x10 ⁻⁰¹	20 ± 4	22 ± 2	20 ± 1	16 ± 2	13 ± 3	15 ± 5
DPPV_[90]zeolite Y (Si/Al=5.1 and NH ₄ ⁺)	dPPV_[90]NH ₄ ⁺ Y		3.82 ± 3.12 x10 ⁻⁰²	2.76 ± 1.80 x10 ⁻⁰¹	1.02 ± 3.58 x10 ⁻⁰¹	31 ± 3	15 ± 4	21 ± 1	10 ± 1	11 ± 2	9 ± 2
DPPV_[90]zeolite Y (Si/Al=5.1 and H ⁺)	dPPV_[90]HY		1.30 ± 8.22 x10 ⁻⁰²	8.61 x10 ⁻⁰¹ ± 4.59 x10 ⁻⁰²	2.20 x10 ⁻⁰¹ ± 2.91 x10 ⁻⁰²	16 ± 7	17 ± 3	17 ± 3	14 ± 1	15 ± 2	11 ± 4