

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

First, poly(p-phenylene vinylene) PPV was synthesized by chemical polymerization and doped with sulphuric acid to produce doped PPV or dPPV. Then dPPV was mixed into zeolites Y three different cations: Zeolite Y (Si/Al=5.1 and NH_4^+) or NH_4^+Y ; Zeolite Y (Si/Al=5.1 and Na^+) or NaY; and Zeolite Y (Si/Al=5.1 and H^+) or HY to detect the three different ketone vapors: acetone; methyl ethyl ketone (MEK); and methyl iso buthyl ketone (MIBK). The effects of dPPV, cation type, and ketone vapor type were investigated. For the effect of dPPV, the electrical conductivity sensitivity of 10%v/v of dPPV mixed with NH_4^+Y increased by an order magnitude under acetone exposure. Thus, the zeolite composite was fabricated with 10%v/v of dPPV to study the effect of cation types (NH_4^+ , Na^+ , and H^+). The highest electrical conductivity sensitivity was obtained with the dPPV_[90] NH_4^+Y under acetone exposure when compared with other composite systems: (dPPV_[90]NaY and dPPV_[90]HY) due to the highest specific surface area of NH_4^+Y . For the effect of ketone types, the dPPV_[90] NH_4^+Y exhibited the highest sensitivity values ($3.82 \pm 3.12 \times 10^{-02}$) towards acetone because of its smallest size .

However, the electrical conductivity sensitivity of the zeolite should be further improved by the ion exchanged process with alkaline cations. Thus, NaY was chosen to study the effects of alkaline cation, cation concentration, and the cyclic interval on the electrical conductivity sensitivity towards three ketone vapors: acetone; MEK; and MIBK at the vapor concentration of 30000 ppm in N_2 . NaY was ion exchanged with K^+ , Mg^{2+} , and Ca^{2+} to prepare 50KNaY, 50MgNaY, and 50CaNaY. The electrical conductivity sensitivity when exposed to acetone vapor was in the order of 50KNaY > 50CaNaY > NaY > 50MgNaY due to the cation size of K^+ > Ca^{2+} > Na^+ > Mg^{2+} . Increasing the cation size in the zeolite framework led to the reduction in the electrostatic interaction between zeolite framework and the cation and the increase in the interaction between the active site on the zeolite and acetone

vapor. Furthermore, the electrical conductivity sensitivity under acetone exposure increased with increasing cation concentration, especially for the 80% mole potassium cation exchange zeolite. The dPPV/[90]80KNaY was suitable to detect acetone vapor due to the smallest size of acetone molecule which could penetrate into the zeolite framework resulting in the highest electrical conductivity sensitivity. For the cyclic interval, the electrical conductivity response decreased with increasing number of cyclic intervals in the acetone vapor exposure due to the irreversible interaction between the zeolite and acetone vapor as evidenced by the FTIR spectrum.

To extend the operation window of acetone vapor detection, at the lower vapor concentration, NaY was developed by the ion exchange with transition metals to prepare 80CuNaY, 80NiNaY and 80FeNaY at 80% and to detect three ketone vapors (acetone, MEK, and MIBK) under the effects of transition metals and vapor concentration. The electrical conductivity response and sensitivity of 80CuNaY were higher than that of 80NiNaY and 80FeNaY when exposed to acetone vapor at the vapor concentration of 30000 ppm in N₂ because the size of Cu²⁺ was larger than Ni²⁺ and Fe²⁺. The large size of cation in the zeolite framework reduced the electrostatic force between the framework and the cation which led to the increase in the interaction between the active site of the zeolite Y and acetone vapor. Moreover, acetone vapor also provided the highest electrical conductivity response and sensitivity due to the smallest size of acetone vapor relative to other ketone vapors. When dPPV was mixed into the 80CuNaY matrix, the minimum vapor concentration of dPPV/[90]80CuNaY towards acetone decreased from 10 ppm to 5 ppm. This system exhibited the higher sensitivity value relative to dPPV/[90]80KNaY under acetone exposure. Thus, dPPV was clearly shown to enhance the electrical conductivity response and sensitivity of the 80CuNaY matrix. The evidences for the irreversible interaction between the active site and the chemical vapors were investigated and provided for by the FTIR spectrum and AFM technique.

To develop the selective properties of zeolite composites, various types of zeolites was chosen to investigate the responses towards organic vapor molecules (acetone, methanol, and n-heptane). Three different zeolites: zeolite Y (Si/Al=5.1 and

Na⁺) or NaY, mordenite (Si/Al=18 and Na⁺) or NaMOR, and 5A (LTA) (Si/Al=1.0 and Na⁺) or Na5A were ion exchanged with copper cation to prepare 80CuNaY, 80CuNaMOR, and 80CuNa5A. During the acetone and methanol exposures, the electrical conductivity response and sensitivity of 80CuNaY showed the highest values relative to 80CuNaMOR and 80CuNa5A due to the lower Si/Al ratio of 80CuNaY. The low Si/Al ratio provided the hydrophilic properties which was suitable to adsorb polar molecules (acetone and methanol). For the non polar molecule (n-heptane), 80CuNaMOR showed the highest electrical conductivity response and sensitivity towards n-heptane vapor because of the hydrophobic properties of the zeolite mordenite. Additionally, 80CuNa5A exhibited the lowest response and sensitivity values when exposed to the three different chemical vapors due to its low surface area. The electrical conductivity sensitivities towards the organic chemical vapors of 80CuNaY and 80CuNaMOR were increased by mixing with dPPV. Moreover, dPPV-[90]80CuNaY could detect the organic vapors at low vapor concentrations: acetone (5 ppm); and methanol (2 ppm) whereas dPPV-[90]-80CuNaMOR could respond at 5 ppm in n-heptane. It could be concluded that adding dPPV definitely improved the electrical conductivity response and sensitivity towards the organic chemical vapors: acetone; methanol; and n-heptane. The interactions between the gas sensing materials and the chemical vapors were identified by FTIR and AFM techniques and shown to be irreversible. Based on the results, the greatest values of the electrical conductivity sensitivity was obtained from: (1) cation types; (2) zeolite types; (3) organic vapor molecule types; and (4) dPPV.

7.2 Recommendations

In this dissertation, there are potentially many methods recommended to enhance the electrical conductivity sensitivity and the selectivity of poly(p-phenylene vinylene) towards the chemical vapors by varying the doping concentration, type of dopant, grafting with other conductive polymers, adding specific functional groups, and modifications into a nano size.

Moreover, the chemical vapor selectivity of poly(p-phenylene vinylene) can be enhanced by blending with various types of porous materials such as zeolites, metal oxides, graphene, and carbon nanotubes.

For the environment pollution point of view, the development of gas sensor device to monitor toxic gases and vapors are needed without the specific receptors. In term of economic interest, the composite sensor should be in the form of film, layer by layer, electro spinning, thin layer coated onto quartz plate, and developed into intelligent toxic gas sensing systems or lab-on-a-chip devices.