유기 증기 측정용 분자체 수정진동자 센서

정 옥진, 김 영한
동아대학교 화학공학과

Molecular Sieve Quartz Crystal Sensor for Organic Vapor Measurement

Ok Jin Joung and Young Han Kim
Dept. of Chem. Eng., Dong-A University

Introduction

One of modification techniques of the quartz crystal sensor for the determination of organic vapor is organic film coating on the surface of the electrode. Yet the organic film coating has problems with its implementation and maintenance in spite of its good selectivity. Because the adjustment of film thickness is difficult, the reproduction of the film-coated sensors is also difficult and the sensitivity of the sensors depends largely upon the film condition. In addition, they are not utilized in the environment of large temperature variation.

Though the control of the film thickness is possible by adopting the LB film technique, other problems associated with the organic film are not solved by the technique. Polymer film coated on sensors improves the stability of the coating and has high selectivity on detected materials. A recent study [1] introduced polymer membrane coating technique to measure fish freshness as a practical application. Using multiple sensors with different polymer coatings, the identification of a certain component is also available.

Carbon coated sensors have high stability and endure harsh environment in application, though they are not selective to organic substances. Kim et al. [2] investigated the stability of a carbon-coated sensor to find that it is very stable and easy to regenerate by simple thermal treatment. The sensor is fabricated from the process under very high pressure, and therefore it is difficult to fabricate and expensive. Chao and Shih [3] introduced a simply prepared carbon sensor. The coating of fullerene (C_{60}) is readily made from dropping a drop of dissolved carbon in solvent and drying without any binding. However, its maintenance is not simple and hard to be utilized in harsh condition.

Though activated carbon is well known for its capability to adsorb most organic substances, it lacks selectivity on the adsorbates. Keeping the ruggedness and stability of the activated carbon, molecular sieve has the selectivity which gives different adsorptivity depending on the molecular size of the adsorbates. Coating the molecular sieve on one electrode of a quartz crystal oscillator is conducted to fabricate a gas sensor in this study. The detection performance of the sensors with two different pore sizes of the molecular sieve is examined from their implement in the determination of methanol, ethanol and n-hexane concentration in air. From the performance test, the ruggedness, sensitivity and selectivity of the sensor are investigated.

Experimental

An AT-cut quartz crystal having base frequency of 8 MHz (Sunny Electronics Co., Korea) is utilized to prepare the sensor. The electrode of the crystal is silver finished. Two pore sizes of 4 and 5 Å molecular sieve (Yakuri Pure Chemical Co., Japan) having pellet size of 1/16 inch is used, and for a binder the phenol resin (Novolac, Dong Kwang Chem. Co., Korea) having average molecular weight of 400, purity of 99% or above and particle size of 200 meshes with 13 % hardener of hexamethylene tetramine is added.

The same amounts of the molecular sieve and phenol resin are mixed and ground in an agate mortar for about 30 minutes. In order to separate fine particles of same size, the ground powder is placed on the bottom of an acrylic column of 20 cm long and 5 cm in inside diameter, and fine particles are blown with air having flow rate of 0.9 L/min. introduced to the bottom of the column through a 5 mm vinyl tube. The particles flown from top of the column are collected on the surface of the crystal for 2 minutes. For the prevention of unnecessary collection of the particles on the surface other than electrode, a holed piece of paper is placed on the crystal surface.

The coated crystal is cured in a drying oven of 160 °C for an hour to make the particles bound on the surface. An SEM photograph of the crystal is exhibited in Figure 1. In the figure, dark particles are binder resin and grayish particles are molecular sieve. At lower left corner there is a large particle of molecular sieve and resin bound. The measurement of frequency change before and after the coating indicates some 10,000 Hz reduction of the frequency.

The prepared sensor is installed in a specially designed cell, and two leads of the sensor are directly connected to an oscillation circuit for the minimum noise to the signal. The oscillation is counted using a home-made frequency counter. The digital signal of the count is provided to a PC for data processing.

The experimental setup is demonstrated in Figure 2. Air is provided from a blower and a portion of the air is vent through a bleeding valve. An objective organic vapor is obtained by passing some of the air to be fed to the measuring cell through an Erlenmeyer flask of 0.2 L capacity containing liquid of the organic substance.

The concentration of the organic vapor in air is determined with a gas chromatograph (Hewlett Packard, Model 5890 Series II). Temperature for the injector, column and detector of the GC is all set at 200 °C. The column is 6 feet long and 1/8 inch in diameter and is filled with the Porapac-Q.

The adjustment of organic vapor concentration is carried out from manipulating the valves installed in the line of gas flow. The flow rate of mixed gas flow during frequency measurement is maintained at 0.4 L/min. all the time by controlling the valve installed at the bottom of the flow meter. Experiment is conducted at room temperature.

Results and discussion

The detection performance of the molecular sieve coated sensor is examined from the measurement of frequency variation when different concentrations of organic vapor contained air are contacted to the sensor surface. While organic vapor contained air flows continuously with constant flow rate of 0.4 L/min., the variation of frequency is monitored and the outcome is analyzed. In order to examine the process of adsorption and desorption of the organic vapor on the molecular sieve coated on the sensor surface, fresh air and organic substance contained air are alternately provided.

Figure 3 shows the experimental result of the determination of methanol with 5Å molecular sieve coated sensor. In the beginning, fresh air is supplied, and then methanol-contained air is delivered. The concentration of methanol is measured by taking the sample of 1 mL with a sampling syringe from the gas flow line and by analyzing it with the gas chromatograph. The decrease of frequency indicates that the coated molecular sieve adsorbs the methanol and there is a mass increase on the sensor surface. After the decrease is settled, fresh air is fed to desorb the methanol adsorbed on the molecular sieve. The frequency increases again, and it returns to a little more than the initial value. Because the experiment is conducted in a flow system, some drift in the base frequency is accompanied. After the frequency with the air is kept at a steady value, sample flow of a higher concentration is introduced to determine frequency variation with different concentration of methanol. These measurements are conducted for four different concentrations of methanol contained air in flow. The incompleteness of frequency recovery with fresh air supply is linearly increased for the last three runs, but the elevation of frequency shift with the increased supply of methanol is distinctive and proportional to the methanol concentration.

In case of ethanol, the outcome of the frequency measurement is illustrated in Figure 4. The sensitivity of the sensor to ethanol contained air is about 1/5 of that of methanol. Because the 5Å molecular sieve is designed for the separation of the molecular size of methanol, ethane and propane or smaller, the 5Å molecular sieve coated sensor gives much less sensitivity with ethanol contained air. Unlike other solid particle coated sensor, such as activated carbon sensor, the molecular sieve coated sensor has selectivity to the molecular size of detecting material. Though some frequency shift is observed with ethanol detection in Figure 6, the difference of the frequency shift between the cases of methanol and ethanol is significant when it is counted that even a blank sensor shows some frequency shift. A blank quartz crystal is installed in the measuring cell and several different concentrations of ethanol contained air is supplied to measure the frequency shift.

When a mixed vapor of methanol and ethanol is applied in order to examine the selectivity of the molecular sieve coated sensor, the frequency variation with three different concentrations of methanol and ethanol is given in Figure 5. In this experiment a mixture of methanol and ethanol in the ratio of 1 to 2 is placed in the flask to produce the mixed vapor. The numbers in parentheses are the ethanol concentration. The frequency shift of the mixture is close to that of methanol in the similar concentration in spite that a little more amount of ethanol vapor is present. Another big molecule of n-hexane is introduced to investigate the selectivity. The frequency shift is less than that of ethanol as expected, though high concentration of the vapor is contained in air.

The outcome indicates that the sensor coated with 5Å molecular sieve satisfactorily discerns methanol vapor from bigger molecules, but it does not separate from smaller molecules. When 4 Å molecular sieve coated sensor is implemented to detect methanol, the same result of measuring ethanol with 5 Å molecular sieve sensor is yielded as shown in Figure 6. In other words, provided that two sensors of the 4Å and 5Å molecular sieve coating are implement at the same time, the determination of methanol from the mixture of various species having different sizes of molecule is available. In addition, the concentration of methanol is found from the relation between concentration and frequency shift, which is obtained from Figure 3. Though a linear relation is not obtained, the possibility of concentration determination from the frequency variation using the molecular sieve coated sensor is shown from the relation.

When it is considered that the experiment of this study is conducted in a flow system, the ruggedness and sensitivity of the sensor are satisfactory for the application in a harsh environment. Because the sensor is produced from thermal treatment, it can be implemented in dry environment unlike an organic film sensor, and the regeneration of the sensor by heat treatment is possible. Also, the sensor is made of readily available materials and fabricated from a simple process, and therefore it is inexpensive.

Conclusion

In order to give selectivity to a solid particle coated quartz crystal sensor having ruggedness and stability with easy maintenance, the coating of two difference pore sizes of molecular sieve on one of electrodes of a quartz crystal oscillator is exercised here. The applicability of the sensor as a gas sensor is examined by monitoring the adsorption and desorption of organic vapors on the molecular sieve. The variation of resonant frequency of the sensor is investigated to explain the adsorption process. The frequency measurement is conducted in a system of flowing air to prove the ruggedness of the sensor for practical implementation.

From the frequency measurement for different concentrations of three different organic substances—methanol, ethanol and n-hexane—contained in air, it is shown that the sensor can detect the concentration of different sizes of organic materials. A good recovery of the sensor to the initial condition is demonstrated, and the ruggedness is proved from implementing the sensor in a flow measurement system. The sensor is produced from readily available material with a simple process, and it is easily regenerated from heat treatment.

Acknowledgment

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References

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[3] Y.-C. Chao and J.-S. Shih, Adsorption study of organic molecules on fullerene with piezoelectric crystal detection system, Anal. Chim. Acta, 374 (1998) 39-46.

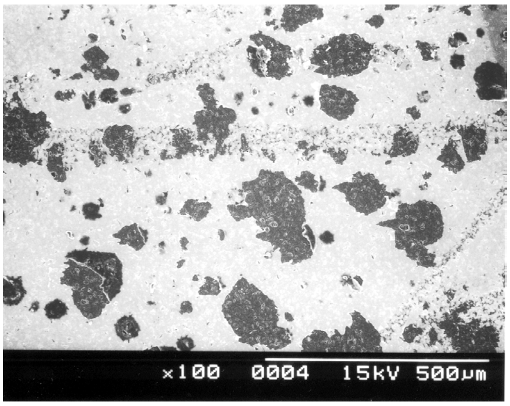

Figure 1. An SEM photograph of molecular sieve coated sensor.

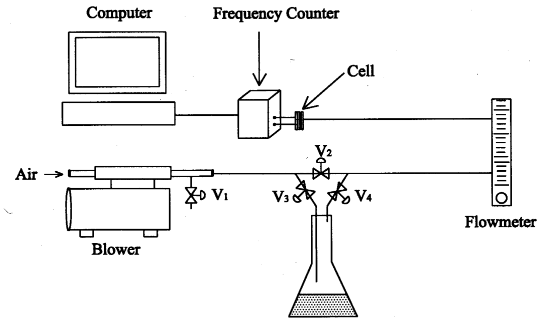

Figure 2. Experimental setup.

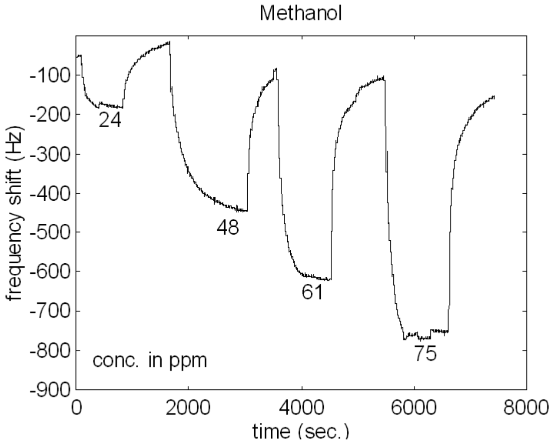

Figure 3. Variation of frequency with various concentration of methanol contained air.

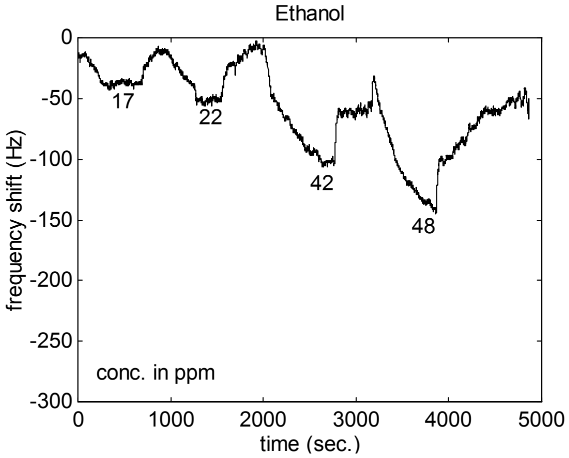

Figure 4. Variation of frequency with various concentration of ethanol contained air.

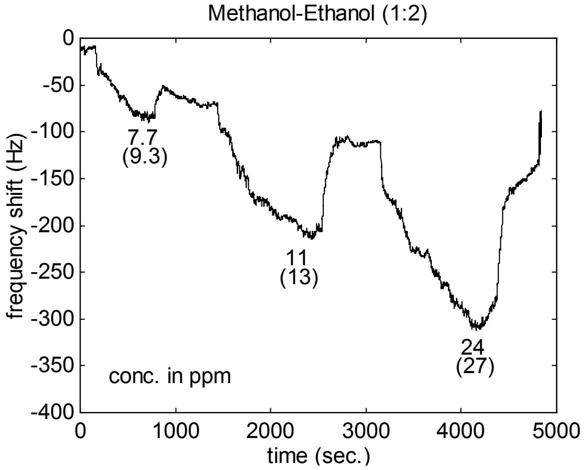

Figure 5. Variation of frequency with various concentrations of methanol and ethanol mixed vapor contained air.

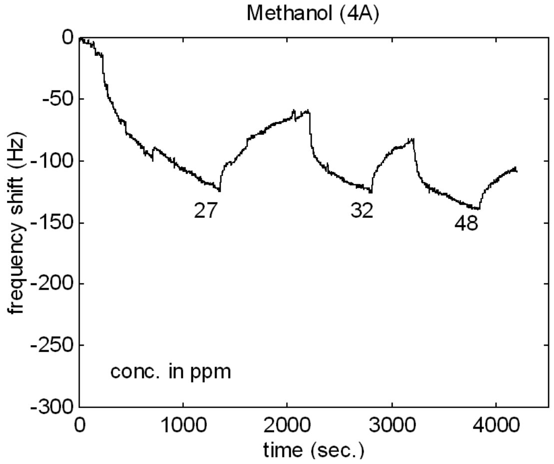

Figure 6. Frequency variation of 4Å molecular sieve coated sensor with various concentration of methanol contained air.