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Gas Sensors Based on Nanosized-Zeolite Films to Identify Dimethylmethylphosphonate

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Gas sensors have been developed using ZSM-5 zeolite films immobilized on a quartz crystal microbalance (QCM). Frequency shifts with different concentrations of nerve agent simulant dimethylmethylphosphonate (DMMP) are measured. The frequency shifts with time at 1 ppm, 5 ppm and 20 ppm DMMP are examined. A minimum detectable concentration of 1 ppm DMMP has been obtained in N_2 at 293 K. In order to improve the selectivity of the sensor to the DMMP from other organic gases, different pore size zeolite films such as ZSM-5 zeolite and Ag^+-modified ZSM-5 zeolite are studied. The frequency shifts of the films to acetone and ethanol at 1 ppm concentration are observed. Using principle component analysis, we can easily identify and quantify these testing gases.

1. Introduction

Today the threat of terrorism represents the greatest threat to the world. Lethal chemical warfare gases, such as sarin (methyphosphonofluoridic acid), are an extremely dangerous threat to public security. The need to detect such gases for warning and alarm is becoming more and more urgent. In this study, dimethylmethylphosphonate (DMMP), a simulant structure of the nerve agent sarin, is detected at very low concentrations using novel sensitive nanozeolite films. Figure 1 shows the similar structures of DMMP and sarin.[(1)]

Zeolites have long been known for their molecular sieving properties based upon their crystalline pore structures with molecular dimensions. They have been widely used as

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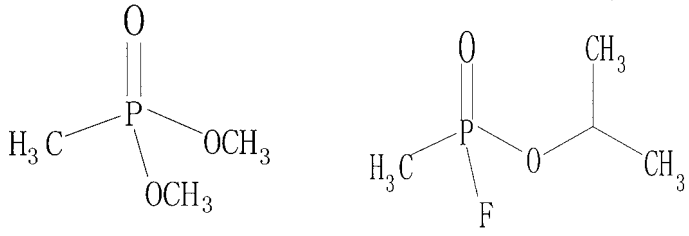

(a) DMMP (b) Sarin

Fig. 1. Structure of (a) the chemical warfare simulant dimethylmethylphosphonate (DMMP) and (b) the warfare agent sarin (methyphosphonofluoridic acid, 1-methylethyl ester).

catalysts, ion exchangers and adsorbents.[2] As for the application of zeolite to sorbents, the nanosized channel system provides a size- and shape-selective matrix for absorbing molecules, while maintaining a high surface to mass ratio. Molecules can be organized within the framework with a high spatial precision on the nanometer scale.[3] These properties are needed for sensitive materials in sensors to detect organic and inorganic gases, such as acetone, ethanol,[4] NO and SO_2.[5] The aim of this study is to realize the efficient detection of DMMP employing nanozeolite materials. Therefore, a new type of ZSM-5 nanozeolite particularly sensitive to DMMP is synthesized and deposited on the mass sensor of a quartz crystal microbalance (QCM).

A QCM is based on a piezoelectric quartz substrate coated with keyhole-pattern electrodes on opposite surfaces of the crystal. The mass change Δm (in grams) per face of the QCM causes proportional shifts Δf in its fundamental resonance frequency F. According to the Sauerbrey equation[6]

$$\Delta f = -2.26 \times 10^{-6} \frac{F^2 \Delta m}{A}, \tag{1}$$

where F (Hz) is the fundamental resonance frequency and A (cm^2) is the electrode surface area. The sensitive film absorbs the detected gas, the mass of the QCM increases and the resonance frequency F decreases. The mass of the absorbed gas can be calculated by measuring the shift in frequency Δf.

2. Materials and Methods

2.1 *Synthesis of ZSM-5 and Ag^+ZSM-5*

Tetraethyl orthosilicate (TEOS, Aldrich), aluminum sec-butoxide (Fluka) and 40% aqueous tetrapropyl ammonium hydroxide (TPAOH, Acros) solutions are used as sources of silica, aluminum, and template,[7] respectively. Solutions of TEOS and TPAOH are mixed by agitation. Aluminum sec-butoxide is slowly dripped into the mixture of TEOS and TPAOH while stirring. Three hours later, deionized water is added to the reaction mixture. The composition of the initial reaction mixture in terms of molar ratio is as follows: TEOS: TPAOH: Al_2O_3:H_2O =9:25:0.25:480. Then, the mixture is transferred into a Teflon-lined autoclave and heated at 100°C for 36 h. After the colloidal zeolite particles are separated from the mother liquid by centrifugation, they are redispersed in deionized

water. This cycle is repeated at least 5 times. The sample is calcined at 550°C for 5 h to remove the TPAOH.

The nano-ZSM-5 powder is introduced into 1 mol/L silver nitrate and mixed at 70°C for 5 h. The Ag^+ZSM-5 zeolite is finally achieved by dextrose deoxidizing the sample.

2.2 *Characterization*

Before applying them to the sensor, the nanosized ZSM-5 zeolite films are charactered by tunneling electron microscopy (TEM). Figure 2 shows the uniform size of ZSM-5 crystals at a diameter of 100 nm under TEM. Figure 3 shows the uniform size of Ag^+ZSM-5 crystals at a diameter of 100 nm under TEM.

After characterization, the nanosized ZSM-5 zeolite is suspended in ethanol (the analyte) and sonicated for 5 min to suspend the nanosized particles. The ZSM-5 is sprayed

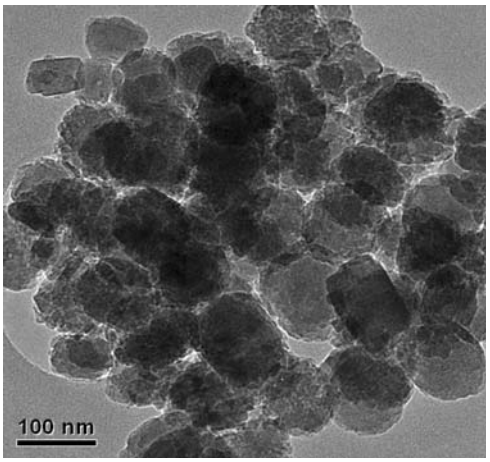

Fig. 2. Image of particles of ZSM-5 under TEM.

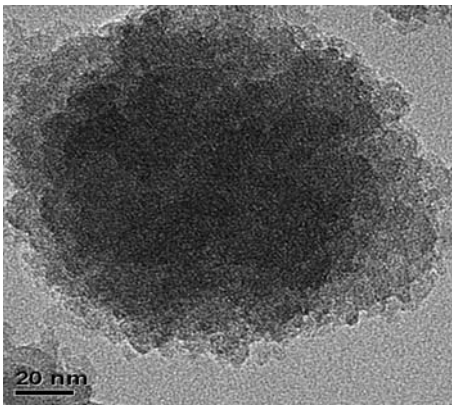

Fig. 3. Image of particles of Ag^+ZSM-5 under TEM.

on each face of the QCM. The thickness of the film is recommended to be between 1 μm and 2.5 μm. If the film is over 2.5 μm thick, the QCM with an 8 MHz fundamental frequency will not function.

2.3 *Experimental method*

Figure 4 shows the experimental apparatus for gas sensing. The QCM coated with nanosized ZSM-5 zeolite films is set in the chamber, which maintained a temperature of 293 K. A thermal energy converter (TEC) is used to remove the humidity from the gas, which seriously affects the precision of gas detection. Before testing, 70 ml/min nitrogen is driven through the chamber until the QCM's frequency shift is controlled to ±2 Hz in 10 min. In this state, we can conclude that the QCM is balanced. Then, the testing gas is applied to the measurement system at the same flow rate and temperature. When the QCM reaches a new balance, the test is over and the testing of another gas begins. Every balance is defined achieving a frequency shift within ±2 Hz. This QCM frequency shift is caused by gas absorption/desorption. A mass flow controller regulates the gas flow at 70 ml/min. The shifts in resonance frequency are measured with a Chi440 instrument(frequency counter/oscillating circuit). Data from the sensor is recorded and the curve of the frequency shift with respect to time at different concentrations of gases is displayed on a personal computer.

To test the sensitivity of the sensors different concentrations of DMMP, pure nitrogen, 1 ppm, 5 ppm and 20 ppm DMMP vapor are applied sequentially to the system.

To test the reproducibility, pure nitrogen and 1 ppm DMMP vapor in nitrogen are applied to the system three times sequentially. To test the desorption temperature of DMMP, temperature above and below the DMMP boiling point 200°C and 120°C are tested, respectively.

Selectivity to the inorganic gases using ZSM-5 zeolite has been reported by Sasaki and Tsuchiya.[5] The ZSM-5 film is not very sensitive to inorganic gas at concentrations less than 10 ppm. To detect the selectivity of the ZSM-5 film to DMMP gas from other organic

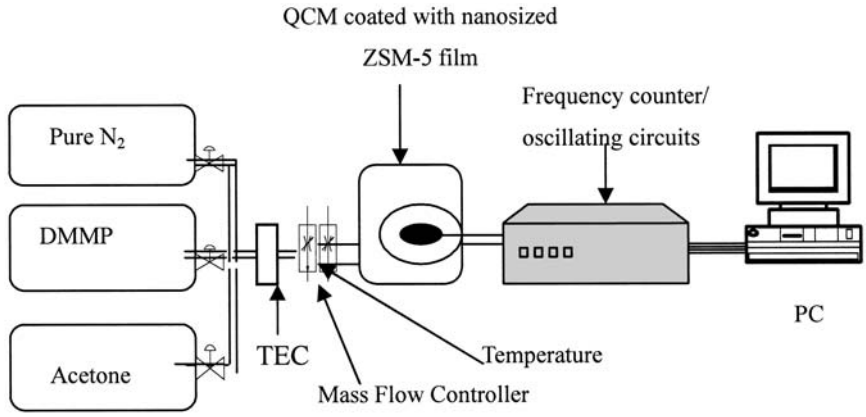

Fig. 4. Diagram of system used for gas sensor based on ZSM-5 elite film.

gases, zeolite ZSM-5 and Ag^+ZSM-5 with different porosities, have been coated on the QCM. Different frequency shift curves characterize the selectivity of the sensor to the organic gases. Acetone (1 ppm) and ethanol (1 ppm) are tested under the same conditions. Using principle component analysis (PCA), we can easily qualify and quantify 1 ppm DMMP gas.

3. Results

3.1 *Sensing experiment for different concentrations of DMMP*

Figure 5 shows the response of a QCM coated with nanosized ZSM-5 to 1 ppm, 5 ppm and 20 ppm DMMP in N_2. It is obvious that the frequency shift gradually increases when 1 ppm DMMP gas flows into the chamber. The base line of the frequency shift after 100 s has shifted from zero to approximately –60 Hz. When the QCM reaches a new balance the 5 ppm DMMP gas is introduced in and the frequency shift increases much more than before. With respect to 1 ppm, 5 ppm and 20 ppm DMMP gas, the frequency shifts are 60 Hz, 80 Hz and 120 Hz, respectively. This result demonstrates that the nanosized ZSM-5 film is very sensitive to low concentrations of DMMP gas. This high sensitivity is due to the poriferous microstructure of ZSM-5.

3.2 *Reproducibility of the analysis*

Figure 6 shows the reproducibility data of the sensor in response to 1 ppm DMMP. The results show reproducibility of the values for the most part, but the frequency shifts differ. As DMMP is a polar molecule, the Coulombic force between DMMP and ZSM-5 is very strong. Consequently it is more difficult to expel the DMMP molecules from the nanopores of the ZSM-5. We can also draw the same conclusion from Figs. 6 and 7, the gradient of the curve for absorption is larger than that for desorption; the response velocity for absorption is higher than for desorption. As a result, the absorption time is shorter than the desorption time.

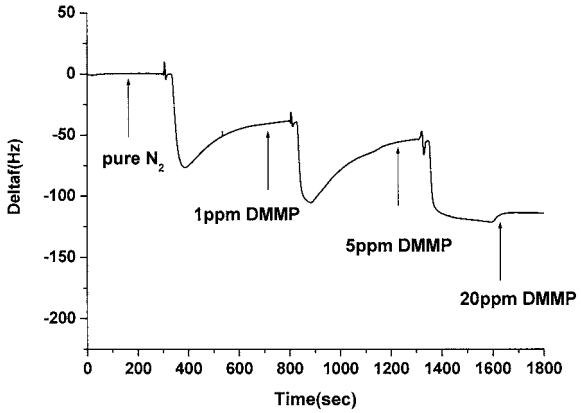

Fig. 5. Dynamic response curve to different concentrations of DMMP gas.

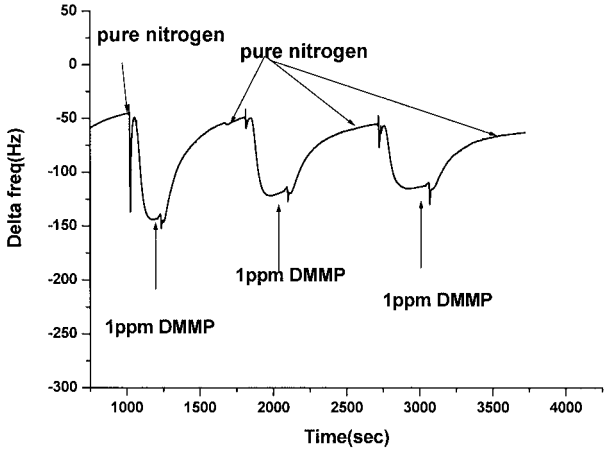

Fig. 6. The reproducibility tests of detection of 1 ppm DMMP. (Pure nitrogen and 1 ppm DMMP gas are detected three times sequentially.)

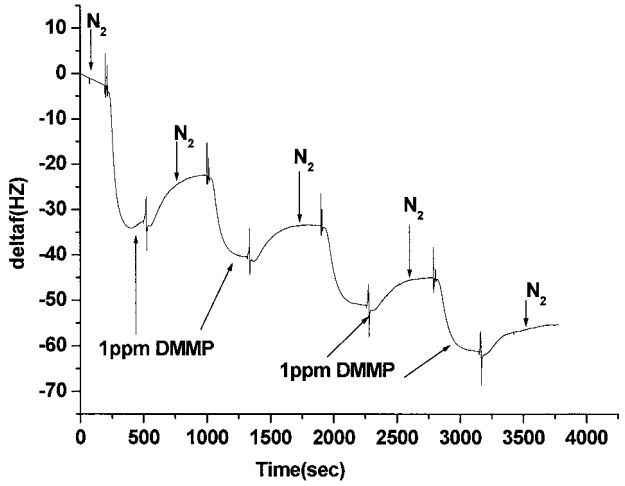

Fig. 7. Dynamic response curve of sensor to 1 ppm DMMP. (The sensor is preheated at 120°C for 3 h.)

As for the velocity of DMMP desorption, the temperature is dominant factor for highly polar DMMP gas. Comparing Fig. 6 with Fig. 7, we can clearly see the trend in the desorption curves. Figure 6 shows the desorption temperature is the DMMP boiling point of 200°C, while Fig. 7 shows a desorption temperature of 120°C. The frequency shift is about 60 Hz in Fig. 7, while the frequency shift is 30 Hz in Fig .7. The adsorption response time is 100 s in Fig. 6 and 200 s in Fig. 7. At the boiling point of DMMP, the DMMP vapor desorbed more completely at a higher temperature, and the molecular activity of the ZSM-5 film can be thoroughly renewed. The frequency shifts much more in Fig. 6 than in Fig. 7. However, if the desorption temperature is much higher than the DMMP boiling point, the lifetime of the sensor decreases.

3.3 *The selectivity of the sensor*

To characterize the selectivity of the sensor, we test the different frequency shifts with sensor coatings of ZSM-5 and Ag^+ZSM-5 films. 1 ppm acetone, 1 ppm ethanol and 1 ppm DMMP are tested under the same condition. Figure 8 shows two sensors based on different porous zeolite films; their sensitivities to the same organic gas are different. At 1 ppm DMMP the frequency shift of ZSM-5 is 80 Hz while that of Ag^+ZSM-5 is 20 Hz. However, at 1 ppm acetone the frequency shift is 50 Hz for Ag^+-modified zeolite, but 30 Hz for ZSM-5 zeolite. The different result is due to the different pore sizes of zeolites. From the TEM images in Figs. 2 and 3 we can easy see the pore size of ZSM-5 is larger than that of Ag^+ZSM-5. Thus, the smaller molecule (acetone) can be absorbed efficient by the Ag^+ZSM-5 zeolite films.

Figure 9 shows the results of PCA on the frequency shifts. PCA is applied to reduce the dimensionality from three to two principal components (PC1 and PC2). The percentages

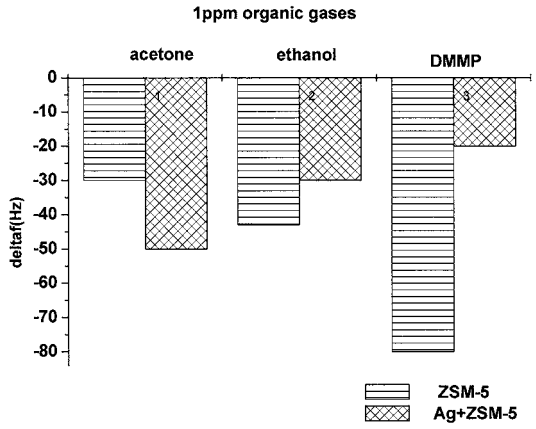

Fig. 8. Frequency shifts with respect to 1 ppm acetone, 1 ppm ethanol and 1ppm DMMP.

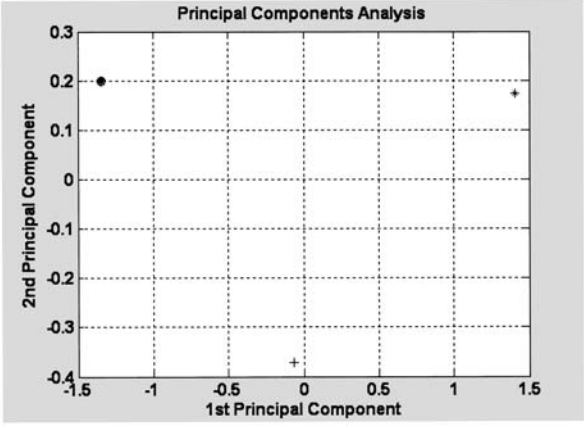

Fig. 9. (· 1 ppm acetone, * 1 ppm ethanol, + 1 ppm DMMP) Result of PCA on the frequency shifts of signal for 1 ppm acetone, 1 ppm ethanol and 1 ppm DMMP.

shown in the figures are the percentages of the total variances. The separately plotted data depending on the gas species suggests that this sensor system could be applied for automatic qualification and quantification using an artificial neural network,[8] which we will carry out in our future work. The results show that 1 ppm DMMP is clearly discriminated from the other DMMP concentrations. 1 ppm DMMP gas is successfully qualified and quantified by the frequency shifts.

4. Conclusion

In summary, the nanosized ZSM-5 zeolite film is fabricated on the QCM, and the QCM is used for sensing 1 ppm, 5 ppm and 20 ppm DMMP gas by measuring frequency shifts. The lowest measured DMMP concentration is 1 ppm. The selectivity is also tested with Ag^{+}ZSM-5 nanozeolite films under the same condition. Zeolite sensors with different porosities have the different sensitivities to organic gases. 1 ppm acetone, 1 ppm ethanol and 1 ppm DMMP have been detected under the same condition by ZSM-5 and Ag^{+}ZSM-5 zeolite sensors.

Using principle component analysis, 1 ppm DMMP can be easily qualified and quantified. The sensor based on nanosized ZSM-5 also shows reproducible responses during experiments with the desorption temperature at the boiling point of DMMP. It indicates that the sensor with elite ZSM-5 could be used effectively as a nerve agent sensor material.

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