Pertanika J. Sci. & Technol. **16 (2)**: 231 - 237 (2008)
ISSN: 0128-7680

Detection of Hazardous Volatile Organic Compound by Using Semiconductor Based Catalytic Pellet

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ABSTRACT

Catalytic pellets that comprise of various compositions of titanium oxide (TiO_2) and tin oxide (SnO_2) as a substrate have been developed for detection of volatile organic compound (VOC). The pellets were tested for gas-sensing properties in the experimental rig at temperature ranges between 100°C to 400°C. The morphological and structural characteristics of the catalytic pellets were investigated by means of a Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD). The results showed that the sensitivity of the pellet decreased at higher compositions of TiO_2. The structural analysis revealed the appearance of $Ti_{0.1}Sn_{0.9}O_2$ phase, rather than TiO_2 phase in the TiO_2-SnO_2 catalytic pellets. The surface morphology of the pellets indicated that the average grain size decreased with the addition of TiO_2.

Keywords: **Catalytic pellet, ethanol vapour sensor, VOCs, semiconductor based sensor, titanium oxide, tin oxide**

ABBREVIATIONS

S	sensitivity	% (percent)
R_{air}	electrical resistance in air	Ω (ohm)
$R_{ethanol}$	electrical resistance in ethanol vapour	Ω (ohm)

INTRODUCTION

One of the major environmental pollutants in the atmosphere is volatile organic compounds (VOC). Among the various types of VOCs benzene, toluene and xylene are confirmed human carcinogens and could cause diversiform cancers (Brickus *et al.*, 1998). VOCs may be released into the environment through industrial activities where they may have been used as raw materials or solvents in the manufacturing or separating process. Due to its effect on humans, the detection and control of VOCs is deemed necessary. The detection becomes more important especially in the indoor environment, because an average person spends more than 80% of daytime in the indoor environment either in the home or in the work place (Srivastava *et al.*, 2000).

Low concentrations of VOCs often cannot be detected by smell, and are usually well below the detection limit of common sensors. Thus, many researches have been carried out to develop VOC gas sensors, especially with the use of tin oxide (SnO_2) as the sensing

Received : 3 March 2008
Accepted : 8 April 2008
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medium. SnO_2 is proven to be one of the most attractive materials for gas sensor application due to its high sensitivity to gas as well as high chemical stability (Senguttuvan *et al.*, 2007). SnO_2 is an n-type semiconductor material, which at typical working temperatures of between 200°C and 450°C, adsorbs oxygen from the surrounding atmosphere to form an electron-depleted zone. Its electrical resistance decreases in the presence of a reducing gas, which reacts with the adsorbed oxygen leading to an increase in the electronic concentration. The measured change in the resistive value of the sensor due to the chemical reaction serves as the sensing signal (Lin *et al.*, 1997).

Lack of selectivity is one of the main drawbacks of the SnO_2 gas sensor. In order to enhance the gas sensing properties, the use of metal catalysts such as Ag, Pt, and Pd has been intensively studied (Yamazoe *et al.*, 1983). In addition, composite type sensors using a mixture of n-type and p-type semiconductors such as ZnO(n)/SnO_2(n) (Yu *et al.*, 1999), and CuO(p)/ZnO(n)/SnO_2(n) (Yu *et al.*, 2001) have been proposed in order to obtain stable interfaces. Among other metal oxides the TiO_2 is well known for its high sensitivity to changes in the surrounding gas composition. Furthermore, the applicability of a gas sensor based on composites of TiO_2-SnO_2 has been demonstrated for catalytic photodegradation of organic contaminants assisted by UV light (Zakrzewska *et al.*, 2007). In the present work, catalytic pellets that comprise of various compositions of titanium oxide (TiO_2) and tin oxide (SnO_2) have been developed for detection of volatile organic compounds (VOC). Ethanol was used as the volatile organic compound. The pellets were tested for their gas-sensing properties in the experiment rig at temperatures ranging between 100°C to 400°C. The morphological and structural characteristics of the catalytic pellets were investigated by mean of Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD).

MATERIALS AND METHODS

Pellet Preparation

An appropriate amount of SnO_2 powder (Acros Organics, 99.9%) and TiO_2 powder (Acros Organics, 99+%) were milled in ethanol for 7 hours by using a ball-mill. The mixture was then dried and pressed into pellets (20 mm diameter and 2 mm thickness) using a hydraulic press machine at 10kPa. The pellets were sintered at 650∞C for 3h in air and cooled to room temperature.

Pellet Characterization

The morphological and structural characteristics of the catalytic pellets were investigated by means of a Scanning electron microscope, SEM (Leo Supra 50VP) and X-ray diffraction, XRD (Philip PW 1710 with Cu Ka radiation).

Sensing Performance

Each catalytic pellet was sandwiched between two copper electrodes in a quartz tube to measure the electrical conductivity and sensing behavior in the presence of ethanol vapour as shown in *Fig. 1.* The two copper electrodes were connected to an I-V electronic circuit to measure I-V characteristics. Firstly, the pellet was heated to 150°C in dry air for 10 minutes in order to exclude the moisture effect in the measurement. The electrical conductivity was measured after equilibrating the pellet in dry air for 30 minutes. The

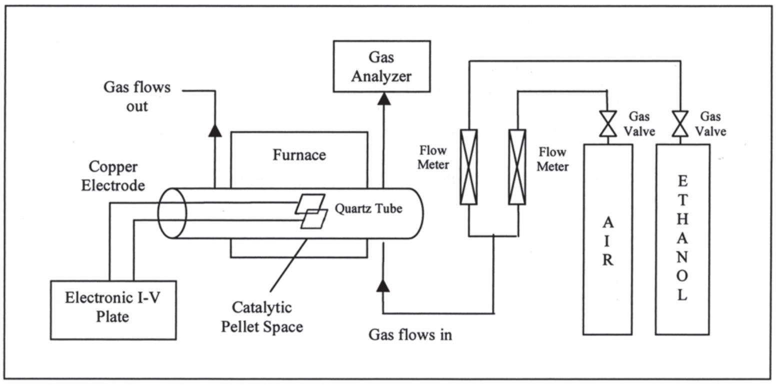


Fig. 1: Experimental rig setup

applied voltage was varied from 15 to 25 V and the resulting current was measured 2 seconds after applying the voltage. The pellet was then kept in dry air for 15 minutes before changing the measurement temperature from 50°C to 300°C. The electrical measurements were repeated after flowing 500 ppm of ethanol vapour in air for 5 minutes. For both sets of measurements, the total gas flow rate was set at 45 cm^3/min. The sensitivity of the sensor pellet to ethanol vapour is defined as;

$$S = \frac{R_{air} - R_{ethanol}}{R_{air}} \times 100\% \quad (1)$$

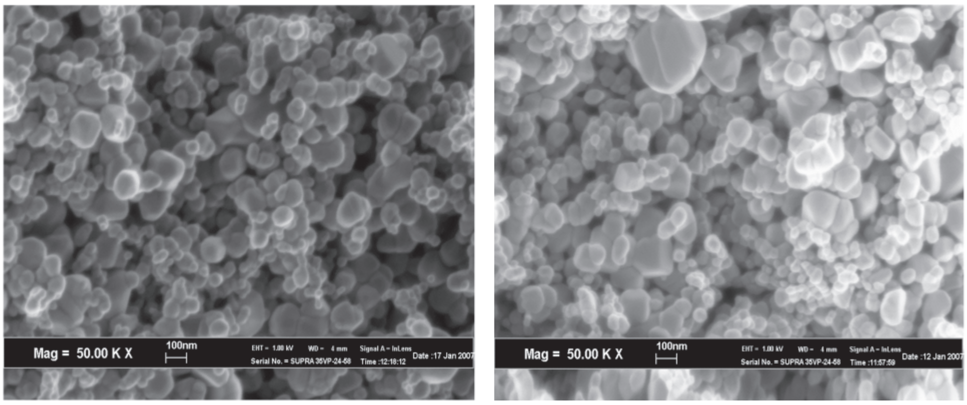
where S is the sensitivity (%), R_{air} and $R_{ethanol}$ are the electrical resistance of the pellet in air (ohm) and in ethanol vapour (ohm) respectively. The pellets' variations in sensitivity against temperature were performed.

RESULTS AND DISCUSSION

Surface Morphology

Figs. 2(a) and *2(b)* show the surface morphologies of pure SnO_2 and SnO_2 with 5 % TiO_2, respectively. It is obvious that the grains in *Fig. 2(a)* are of relatively uniform size, while there are two sizes of grains present in *Fig. 2(b)*. The larger sizes are the SnO_2 grains and the smaller size grains are those of TiO_2. It can also be observed that the grain size decreased when 5wt% of TiO_2 was added. It seems that by adding TiO_2 grain growth was hindered. Zhu *et al.* (2006) made similar observations in ZnO-based varistor. When TiO_2 was added more grains clogged together. It seems that TiO_2 not only reacts with SnO_2 to form another phase along the grain boundaries but also diffuses into the bulk grain.

In order to identify the phases of the sample, XRD was used and the diffraction patterns obtained as shown in *Fig. 3* for the sample that was sintered at 650°C for 2 h. It was found that the sample has a spinel structure which is the $Ti_{0.1}Sn_{0.9}O_2$ (blue colour) phase. In addition to $Ti_{0.1}Sn_{0.9}O_2$, only the SnO_2 phase (red colour) is detected. It can be concluded that the SnO_2 nanoparticle reacts with TiO_2 at sintering conditions to form the composite.



(a) (b)

Fig. 2: Surface morphology of catalytic pellet: (a) pure SnO_2, (b) SnO_2-5% TiO_2

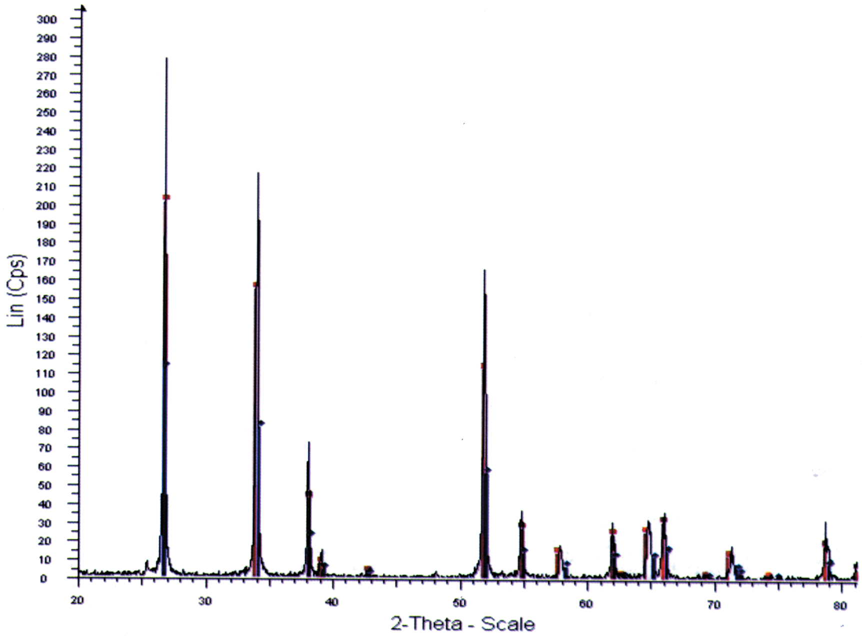


Fig. 3: X-ray diffraction patterns of 5 wt% TiO_2-SnO_2 catalytic pellet sintered at 650°C for 2 h

Fig. 4 shows the X-ray diffraction pattern of SnO_2 catalytic pellets that have 1, 5 and 10 wt% of TiO_2. It can be observed that there are sharp diffraction peaks which indicate the samples have a high degree of crystallization.

Ethanol Sensitivity

The effect of TiO_2 addition on SnO_2 catalytic pellets on gas sensitivity to ethanol vapour was studied in this work. The sensitivity of the catalytic pellets to ethanol vapour is shown in *Fig. 5*. It was observed that the catalytic pellet of 1wt% TiO_2-SnO_2 has the highest sensitivity. The optimum detection temperature is about 250∞C. *Fig. 5* also shows that sensitivity increases with temperature before it reaches its maximum value. The increase in sensitivity with operating temperature can be attributed to the fact that the thermal energy obtained was high enough to overcome the activation energy barrier of the reaction, while the reduction in sensitivity was due to the difficulty in exothermic vapor adsorption (Chang *et al.*, 2002).

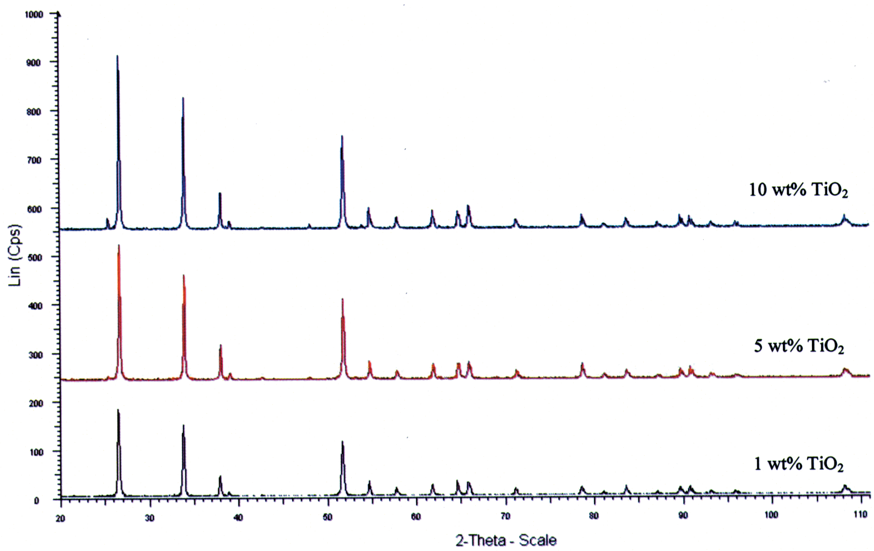


Fig. 4: X-ray diffraction patterns of the catalytic pellet with different TiO_2 contents sintered at 650°C for 2 h

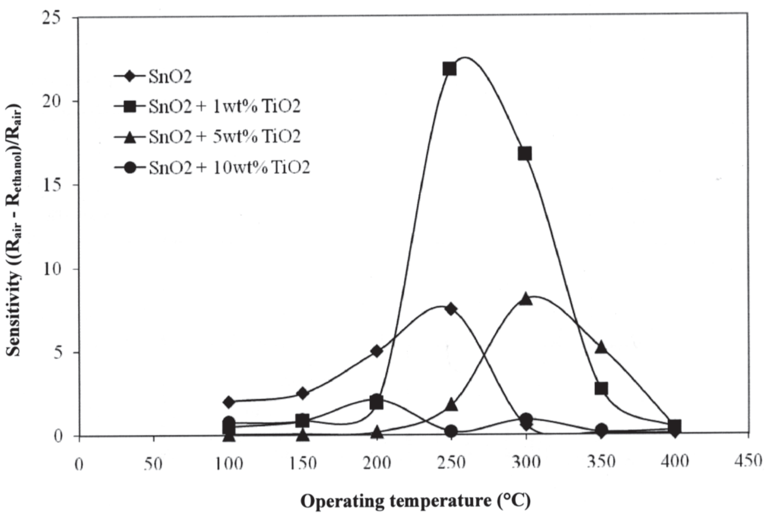


Fig. 5: Sensitivity of ethanol detection at various temperatures

The resistance change is controlled by the species and amount of chemisorbed oxygen on the surface thus the gas sensing mechanism of SnO_2 based sensors belong to the surface controlled type. It is proposed that the the oxidation of ethanol takes place via two routes, one the dehydrogenation to acetaldehyde as shown in Eq. (2) and the other, the dehydration to ethylene as given by Eq. (2) in which [O] represents the surface oxygen ions.

$$[O] + C_2H_5OH\ (gas) \rightarrow CH_3CHO + H_2O \quad (2)$$

and

$$[O] + C_2H_5OH\ (gas) \rightarrow C_2H_4 + H_2O \quad (3)$$

The oxidative hydrogenation reaction is mainly catalysed on the basic sites and dehydration is favored on the acidic sites. It is known that the first one has more sensitivity than the latter. The intermediate products, acetaldehyde and ethylene are subsequently oxidized to carbon dioxide and water (Vaishnav *et al.*, 2005).

As mentioned earlier, the addition of a small amount of TiO_2 altered the structure of the SnO_2 catalytic pellet and enhanced the chemisorption of oxygen on the surface. However, this behaviour only occurs at low amounts of $TiO_{2.}$ When the percentage of TiO_2 was increased to 5% and 10%, the sensitivity reduced remarkably. This could be due to the reduction of pellet porosity, which may retard the adsorption of oxygen.

CONCLUSIONS

Catalytic pellets that comprise of various compositions of titanium oxide (TiO_2) and tin oxide (SnO_2) have been developed for detection of VOC. Surface morphology showed that the catalytic pellet has a porous structure. The results also showed that the sensitivity of the catalytic pellet to ethanol vapour increases when 1 wt% of TiO_2 was added.

ACKNOWLEDGEMENTS

The authors are thankful to the Malaysian Ministry of Science, Technology and Innovation (MOSTI) for providing the Long-term Science Fund (6013303) research grant.

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