Journal of Industrial and Engineering Chemistry 29 (2015) 321–329

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Development of metal-loaded mixed metal oxides gas sensors for the detection of lethal gases

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ARTICLE INFO

Article history:
Received 22 January 2014
Received in revised form 13 August 2014
Accepted 31 October 2014
Available online 23 April 2015

Keywords:
Toxic gas
Gas sensor
Screen-printing
Sol–gel
Thick film

ABSTRACT

The gases which may be lethal to humans through short-term exposure in laboratories or industrial settings may paralyze the olfactory sense and impose severe damage to the central nervous system and lungs. This study concerns gas sensors which allow individuals to avoid toxic gases that may be generated in spaces with residues of organic waste with a temperature at 50 ?C or above. We investigated the response and selectivity of the sensors to kinds of toxic gases such as hydrogen sulfide, and acetaldehyde. We also tracked operating temperatures and catalysts. The thick-film semiconductor sensors that detect some toxic gases were fabricated using WO_3/SnO_2 and SnO_2/WO_3 and these were prepared via sol–gel and precipitation methods. The nano-sized SnO_2 powder was mixed with various amounts of metal oxides (SnO_2, WO_3) and doped with transition metals (Pt, Ru, Pd, Ag, Au, and In). The metal-oxide thick films were prepared on an Al_2O_3 plate with a Pt electrode and a Ni–Cr heater via screen-printing method. Morphology, composition, particle sizes, specific surface areas, and phases of sensor materials were investigated by SEM/EDS, BET, and XRD analyses. The measured responses to various lethal gases is defined as the ratio (R_a/R_g) of the resistance of the sensor film in air to the resistance of the film in a toxic gas. The results indicated that the highest response and selectivity of the sensors for toxic gases occurred with doping with 1 wt% of various transition metals and 5–20 wt% WO_3 to SnO_2 at the optimum operating temperature range from 200 ?C to 300 ?C.
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Introduction

Most people living in the present day have a variety of conditions that allow them to live better life than they would have in the past under poorer conditions. As the quality of life improves rapidly, the concern with health and the environment has increased. However, such rapid growth is accompanied with many negative consequences. For example, our living environment is exposed to various toxic gases. The indoor pollution of volatile organic compounds (VOCs), such as benzene, toluene, acetaldehyde, and formaldehyde, has been recognized as the principal cause of many diseases including asthma, emphysema, allergies, and cancer, and received more and more public concern these days [1–5].

Hydrocarbons, oxidized hydrocarbons, nitrogen oxides and sulfur oxides are common air pollutants in everyday living. Among those, Toxic gases generated from organic solvents used in industrial and laboratory processes are becoming an increasing social concern since those materials have a direct impact on the human body. When the human body has prolonged exposure to toxic gases, leukemia, disorders of the central nervous system, and reproductive dysfunction can occur [6–8].

Acetaldehyde and formaldehyde are known to be two of the most widely air-disseminated carbonyl compounds. Aldehydes, which are generated by combustion and oxidization, are produced in to the photochemical reactions that produce ozone, increase global warming, and destroy the ozone layer in the stratosphere. Aldehydes usually exist in a gas phase at room temperature and can remain in the air for a long time. Acetaldehyde is the main source of toxic materials generated in new houses and can appear in the air both indoors and outdoors. Individuals exposed to aldehydes risk having serious toxic reactions caused by the irritation of respiratory organs such as the throat, nose, and bronchus. More serious risks include

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http://dx.doi.org/10.1016/j.jiec.2014.10.048
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having an anesthetic effect on the central nervous system, and, in excessive cases, extreme physical reactions such as paralysis, respiratory disorders, and even the onset of a comatose state [9,10].

Acetaldehyde is extremely irritating in high concentrations (>50 ppm) and it is a probably carcinogen, even though it smells like sweet fruit at low concentrations (odor threshold is about 100/200 ppb). Since its boiling point at atmospheric pressure is 20.2 °C it is an extremely volatile liquid, hence an important acetaldehyde vapor pressure is established in air even when produced in liquid phase. Therefore, exposure to potentially dangerous concentrations of acetaldehyde (8-h exposure limit is 25 ppm—source: OSHA) can occur both indoor and outdoor [11]. Therefore, for both environmental and for health reasons, it is very important to detect the presence of aldehydes.

Hydrogen sulfide is a very toxic gas, and it is dangerous to be in a closed space with active decomposition of organic matter without respiratory protective equipment. During the French Revolution, many deaths were reported in the underground sewage of Paris. According to the National Institute for Occupational Safety and Health (NIOSH), hydrogen sulfide is a causative material for sudden death in the workplace. Since hydrogen sulfide is quickly oxidized into sulfides easily transpired through the kidney, it is not known to have an accumulated toxic effect. The lethal toxins of hydrogen sulfide after the intake of 1000–2000 ppm paralyze the respiratory center and result in stopped breath. At higher concentration levels of 500–1000 ppm, the carotid body is stimulated by the hyperpnea and falls in the sleep apnea state. At lower concentration levels of 50–500 ppm, hydrogen sulfide acts as the primary stimulant to the eyes and respiratory system. The continuous exposure to 250–600 ppm may result in pulmonary edema.

Hydrogen sulfide (H_2S) is an unwanted and toxic by-product of the coal, coal oil, and natural gas industries. When hydrogen sulfide is emitted into the atmosphere, it is converted to SO_x, which is a precursor to acid rain. Accordingly, there is increasing demand for sensing devices that monitor low H_2S concentrations [12,13].

In this study, catalyst-loaded metal-oxide gas sensors were developed which can detect acetaldehyde among many lethal gases, and can also detect hydrogen sulfide as hazardous gas to human body.

Experimental

Preparation of sensor materials

Gas sensors usually have the disadvantage of high electrical consumption because they require a high operating temperature. To mitigate this disadvantage, it is required to increase the electronic conductivity of the sensor materials so that the operating temperature can be lowered. One way to improve electronic conductivity is to add conducting material to sensor materials.

For the acetaldehyde gas sensor, we synthesized WO_3 via a sol–gel process and used it as a sensing material to detect acetaldehyde gas. To enhance the essential functions of sensitivity and selectivity of the gas sensor, metal catalysts were added via the impregnation method [8,9,14]. Transition metals of Pd, Pt, Ru, and In were weighed to give weight ratios of 1–5 wt%, and 1 ml of hydrochloric acid with distilled water was added to completely dissolve the metal catalysts in a beaker. We obtained WO_3 powder or SnO_2/WO_3 powder containing metal catalysts via impregnation followed by heating and stirring the solution with a magnetic stirrer. Then, we dried the solution for 12 h at 100 ?C and calcined it for 2 h at 500 ?C to get powder. Finally, we obtained a fine powder of the sensing material by crushing the crude material.

In the case of the hydrogen sulfide sensor, we added metal catalysts to WO_3/SnO_2 powder to prepare the sensing material by using the same methods described above, among which are the various methods such as the co-precipitation, allegation and impregnation methods [14]. We put metal catalysts of Pd, Au, Ru, In and Ag into the beaker after the weight ratio was set as 0.5–5 wt% and then added 1 ml of HCl to completely melt the metal catalyst. WO_3/SnO_2 powder was added to impregnate the metal catalysts and then slowly heated while stirring with the magnetic stirrer to prepare the metal-catalyst-loaded WO_3/SnO_2. The prepared material was then dried at 110 ?C for 24 h and calcined at 600 ?C for 2 h. Finally, the powder was pulverized to prepare each of the final sensor materials.

Fabrication of thick film

To support the sensing material, a commercial Al_2O_3 substrate with dimensions of 13 mm × 8 mm × 0.67 mm, built-in Pt electrodes in 0.5 mm intervals, and Ni–Cr heater was used. Before coating the thick film, the substrate was put through the washing process, using acetone and heat treatment at 300 ?C, to remove the contaminating substances. After passing through the above process, the sensor paste was coated in a 30 μm thickness via the screen-printing method. Fig. 1 shows a diagram for the fabrication of thick film on Al_2O_3 substrate and a figure of the sensor after the thick film was coated [15].

Analysis of sensitivity characteristics

After we installed the gas sensor at a distance of 50 mm from the bottom of a 10 L (250 mm × 200 mm × 200 mm) chamber, we measured the sensitivity of the gas sensor in the temperature range of 200–400 ?C. In order to remove the electrons in the device, a stabilization procedure was carried out for 12 h at the same temperature as the one used for measurements. After the target gas was introduced into the chamber with the fan on, the resistance was measured with an electrometer after the equilibrium concentration was reached. The sensitivity of the sensor was defined as the ratio of electrical resistance (R_g) after the injection of target gas to the electrical resistance (R_a) in the air, or R_a/R_g. Fig. 2 displays the experimental apparatus used to measure gases in this study.

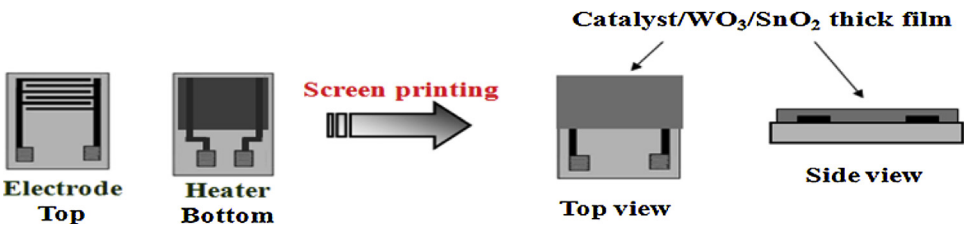

Fig. 1. Structure of thick film sensor.

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