



Sensors based on Ag-loaded hematite (α -Fe₂O₃) nanoparticles for methyl mercaptan detection at room temperature



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ABSTRACT

Sensors based on Ag/ α -Fe₂O₃ nanoparticles have been prepared by the coprecipitation method for sensing methyl mercaptan at room temperature. X-ray diffraction patterns of samples matched perfectly with characteristic peaks of hematite with no peaks assigned to Ag even at the highest concentration. STEM images and EDX analysis revealed the presence of Ag nanoparticles (from 2 to 5 nm) which were highly dispersed onto α -Fe₂O₃ surface with an Ag/Fe ratio from 0.014 to 0.099. The Ag nanoparticles were deposited on the hematite surface. Sensing tests of Ag-loaded hematite nanoparticles showed much higher response signal than the unmodified sensor. Hematite loaded with 3%(Wt) Ag showed the highest response with a linear dependence from 20 to 80 ppm. The sensor also depicted a good selectivity and stability during 4 days with short recovery time. The high dispersion of reduced Ag evaluated by XPS analysis played an important chemical role in the sensing mechanism that favored the contact of CH₃SH with oxygen.

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1. Introduction

Methyl mercaptan (CH₃SH) is a quite well gas known as a standard additive of some gases as natural gas and propane to facilitate the detection of a gas leak and it is also used in ventilation operation systems to alert mine operators of an emergency. The recommended airborne exposure is 0.5 ppm over an 8-h work shift, not to be exceeded at any time [1]. At higher concentrations, that may be encountered in a laboratory, the gas can cause irritation to the eyes and throat, drowsiness and even bronchitis [2]. The gas can be found in paper and pulp mills and it occurs naturally in some vegetables as onions, garlic, and also in coal tar and petroleum distillates. It is used as an intermediate in the production of pesticides, fungicides, jet fuel and plastics and in the synthesis of methionine as well as a gas deodorant for natural gas, propane and butane [3,4]. The design of an appropriate sensor for rapid

measurement of low concentrations of methyl mercaptan demands the development of highly selective sensors with easy manipulation and good reliability.

Different sensing materials have been tested for detection of methyl mercaptan like yttria-stabilized zirconia (YSZ) [5], electronic nose [6], fluorescein mercury (II) acetate (FMA) [7], oxygen sensitive optical fiber [8], among others. Even though these devices present high signal response, the starting material is not accessible and the operating temperature is usually high. As a consequence, previous usage of energy is required and limited.

Metal oxides are the most suitable materials for gas detection due to their irreversible chemical transformations at the surface which allowed them to change their resistance when a testing gas is applied [9]. Particularly, iron oxide as hematite has been used as a sensor in many applications for its semiconductor properties [10–12]. Hematite was applied in different forms: as solid and hollow spindles to sense 2-propanol and acetone [13], as porous α -Fe₂O₃ nanospheres to detect glycine [14], as nanorods via the coprecipitation of FeCl₃ with NaOH solutions to detect rhodamine B colorant [15], as an iron oxide thin film grown by atomic layer

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deposition to sense O₂ and CO [16], as porous Fe₂O₃ nanostructures to measure H₂S concentrations [17], among others. Hematite has proved to be an interesting material for gas sensing applications, but its use at high working temperatures (normally higher than 25 °C) has restricted its potential applications [16]. The semiconductor properties of hematite in addition to the nanosized distribution of its particles are expected to increase the specific surface area and adsorption activity [18–20]. In order to improve sensitivity and stability for practical applications, hematite is usually loaded with some noble metals such as Au [21], Pd [22,23] and Ag [24], which are claimed to create active sites through electronic and chemical sensitization [25].

Some greenhouse gases such as CO and LPG have been tested with sensors based on α -Fe₂O₃ [16,18,20,23]. In these works, the operating temperatures of the sensor material have been usually higher than 150 °C and the preparation method required long-term treatments and high-cost precursors. The challenge in this paper was to apply a feasible low-cost hematite sensor to detect methyl mercaptan operating at ambient temperatures with high sensitivity and stability, also using Ag which is a cheap noble metal. As far to our knowledge, the application of Ag-modified hematite for the detection of methyl mercaptan is novel and the purpose of this work was to correlate the preparation, structure and texture variables of sensor samples with their response signal and selectivity. To this aim, some sensors based on Ag/ α -Fe₂O₃ nanoparticles were prepared for the detection of methyl mercaptan and the role of interaction between the nano-sized hematite and the metal in the sensory properties was explored.

2. Material and methods

2.1. Preparation of Ag/ α -Fe₂O₃ nanoparticles

All chemicals used were analytical grade. Ag/ α -Fe₂O₃ nanoparticles were prepared by the co-precipitation method from 0.1 mol L⁻¹ Fe(NO₃)₃·9H₂O (MERCK, 99%) and 0.5 mol L⁻¹ AgNO₃ (ALDRICH, 99.99%). Mixed solutions of metallic salts (in specific proportions) were added dropwise to an aqueous solution of 0.3 mol L⁻¹ Na₂CO₃ (anhydrous, MERCK, 99.9%) with 0.2 wt% polyethylene glycol, used as a surfactant agent, under vigorous stirring at 80 °C [24]. Afterwards, to the prepared metallic solution, an additional quantity of enough sodium carbonate was added to the prepared metallic solution in order to obtain a pH up to 9.8 [25]. The obtained solution was continuously stirred for 2 h and then, it was aged for 12 h at room temperature. Finished the aging time, the precipitate was filtered, washed with deionized water and dried for 1 h at 120 °C. Then, the solid powder was calcined at 400 °C for 1 h at a heating rate of 2 °C per minute [16]. This procedure pursued to stabilize the material sensor in order to prevent changes in the response signal for the operating conditions. In fact, mesoporous α -Fe₂O₃ and samples based on Ag/ α -Fe₂O₃ with different amount of Ag (from 1.0 to 5.0 wt%) have been prepared.

2.2. Preparation of alumina supports

All the prepared samples were coated onto an alumina support, Fig. 1a. The support dimensions were adjusted to be used in the experimental setup, designed to test gas sensor materials. Geometric dimensions of supports were 25mm×25mm×2mm (Fig. 1b). On the front side, four interdigital gold electrodes of 0.5 mm of thickness were fixed (Fig. 1b). The geometry of the sensor has been designed to maximize gas-solid contact [26]. The material sensor was dispersed in ethylene glycol to make up an impregnation paste which was applied over the alumina surface by the screen printing technique [27], Fig. 1a. In order to stabilize and attach the active

phase onto gold electrodes, the sensor was slowly heated at 2 °C/min and held at 400 °C for 8 h, allowing complete solvent evaporation.

2.3. Experimental set-up to test sensors

Sensors have been tested in the experimental set-up showed in Fig. S1. The system consists of 3 sections:

- A feed section containing two mass flow controllers, one for standard methylmercaptan (LINDE 1% in N₂) and the other one for compressed dry air (<5 ppm of H₂O), LINDE 99% used as a dilution gas to obtain working concentrations ranging from 20 to 80 ppm.
- An analysis section equivalent to a gas chamber with hermetic lock where alumina-deposited sensor was assembled over Ni–Cr resistance and connected online with a Semiconductor Device Parameter Analyzer Agilent B1500A to measure the electrical resistance. The chamber has a duct at the entrance and at the exit through producing gas feed transportation in and out of the system. The gas composition at the exit of the gas chamber was evaluated by an on-line gas chromatograph (VARIAN 450-GC) provided with TCD and FID detector.
- A recorder section for the acquisition and analysis of data using the software Start Easy Expert (Fig. S1).

In the experimental essays, one of the pair of the electrodes has been used as a reference material. In order to clean all the environmental interferences placed over the sensor surface and inside the analysis camera, the electrode surfaces of sensors were previously washed using nitrogen with a flux of 100 cc/min for 2 h. Some previous electrical tests were made applying a voltage work scale from 0 to 10 V with a step of 0.1 V and applying a current frontier of 100 mA to verify the linear dependence of output signal I as a function of V.

Each electrical response of sensors was calculated as the ratio % $\Delta R/R_{\text{air}}$, where ΔR is the difference between response signal measured in the presence of gas (R_{gas}) and air (R_{air}). After each experimental acquirement, a flux of nitrogen was passed through the system to clean the surface.

The samples were characterized by the following techniques:

- Thermogravimetric and Differential Scanning Calorimetry (TG-DSC) analysis were performed using a TA Instrument SDT Q600 to study the thermal treatments of sample preparation. Therefore, Ag-loaded hematite samples were analyzed in a nitrogen atmosphere for temperatures from 25 °C up to 600 °C, with a heating rate of 10 °C/min.
- XRD analysis was performed to study the crystallographic structure of the material. Analyses were made using a diffractometer RIGAKU (Miniflex600) operating with the following parameters: Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), 15 mA, 30 kV, Ni filter, 2 θ scanning range 4–70°, and scan step size of 0.04° per second. The crystal phases were identified using PDF2 database from International Centre for Diffraction Data (ICDD). The mean crystallite sizes were estimated from the Scherrer equation and the selected reflection peaks were fitted by a Gaussian function.
- The textural properties of solids were studied by N₂-sorption measurements at liquid nitrogen temperature using a Micromeritics GEMINI VII-2390t instrument. Prior to the adsorption experiments, the samples were degassed under vacuum by helium at 250 °C for 3 h. The specific surface area was calculated according to the BET method. Also, the pore size distribution and the mean pore size were evaluated using the BJH (Barrett-

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