Research paper

Au/MOx (M = Zn, Ti) nanocomposites as highly efficient catalytic filters for chemical gas sensing at room temperature and in humid atmosphere

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ABSTRACT

Metal oxide supported gold nanoparticles (Au/MOx) have been prepared using deposition-precipitation with urea (DPU) method on commercial ZnO and TiO$_2$ powders. These Au/MOx nanocomposites have been characterized by X-ray powder diffraction, high resolution transmission electron microscopy, nitrogen adsorption-desorption isotherms, and inductively coupled plasma atom emission spectroscopy. They have been used at room temperature as catalytic filters for CO oxidation in humid atmosphere (RH 40%). The CO removal efficiency has been evaluated using metal oxide gas sensors (MOS) device. The catalytic performances assessment of these Au/MOx nanocomposites highlights the efficiency of the Au/ZnO system. An integrated sensing device comprising the gas sensor and its catalytic filter has been developed. In that case, a plastic holder filled with low amounts (50 mg) of Au/ZnO catalytic filter is simply placed above the MOS sensor. This system allows the improvement of the selectivity of the MOS sensors towards other gases, i.e. propane. The presented setting can be applied as one of valuable addition for multi-array sensor devices.

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1. Introduction

Semiconducting metal oxide sensors (MOS) are one of the most widely used sensors for gas detection. Many studies in this area are still ongoing to improve the sensitivity and the selectivity of the MOS sensors. Some strategies to achieve better performances have been suggested. Among them, the use of mixed metal oxide compositions and/or size- and shape- controlled structures (nanoparticles, nanorods, hollow microspheres...) has been proposed [1–6]. Another strategy is to dope the sensitive layer with noble metals such as Pt, Pd, or Au [7,8]. A more recent approach consists in modifying the gas mixture before it reaches the sensitive layers by using catalytic filters which selectively remove CO by oxidation, for example [7,9]. Since MOS sensors are not sensitive to CO$_2$, it is therefore possible to remove CO signature from a gas mixture. These strategies are complementary and can be combined to develop electronic nose consisting of an array of sensors having very distinct detection performances [10–12]. The processing of multivariate signals in sensor arrays allows interpreting and distinguishing between various odors, odorants, and pollutants. It is thus possible to recognize the composition of gas mixtures [13].

One of the most interfering gases is undoubtedly carbon monoxide which is of great importance for electronic nose area. Moreover, this gas has been extensively studied because of the large number of industrial processes which produce CO and the importance of its removal from effluent streams, in particular from exhaust gases [14]. Conversion of carbon monoxide has already been reported using metal oxide supported noble metals such as Pt, Pd, Ru, Rh, and Au owing to their high activity [15,16]. Among such noble metals, the catalytic properties of Au deposited on metal oxide supports have been highlighted by the pioneer work of Haruta in the late 80's [17]. Small Au nanoparticles (NPs) with a typical size below 5 nm and supported on metal oxides such as α–Fe$_2$O$_3$, ZnO, ZrO$_2$, Co$_3$O$_4$, MgO, CeO$_2$, MnO$_2$, TiO$_2$, γ–Al$_2$O$_3$, or SnO$_2$, have been investigated and exhibit a very high catalytic activity for CO oxidation at lower temperatures than other noble metals [18,19]. The effect of

low levels of moisture on catalytic activity of these catalysts has been investigated [20–23]. It has been found that Au/ZnO catalysts exhibit excellent catalytic activity towards CO oxidation in moderate humidity conditions (0.5% CO with 10% O_2 and 1.8% H_2O balanced with argon) [22]. However, there are still no results in the field of CO oxidation at room temperature and in tests conditions typical for gas sensors (*i.e.* with a relative humidity (RH) as high as 40%).

In this paper, we report on the preparation of highly efficient Au/ZnO and Au/TiO$_2$ (1% wt. Au) catalytic filters using the deposition-precipitation with urea (DPU) method [24,25]. We highlight the performance of metal oxide supported gold nanoparticles (Au/MOx) for gas sensing applications at room temperature and in humid atmosphere. To the best of our knowledge, no example has been reported yet on the use of this method for the preparation of Au/MOx nanocomposites in gas sensing field. Preliminary studies performed with catalytic filters placed in a quartz tube upstream of the measurement cell on the gas line highlight the superior catalytic activity of Au/ZnO nanocomposite for CO oxidation. In order to develop an integrated and miniaturized sensing device the Au/ZnO catalytic filter has been placed in a plastic cap which is directly connected above the MOS sensor. Finally, performance of this device has been evaluated under controlled gaseous levels (100 ppm CO, 100 ppm C_3H_8 and a mixture of 100 ppm of CO and C_3H_8) at room temperature and in humid atmosphere (40% RH).

2. Experimental

2.1. Catalysts preparation

Prior to use, zinc oxide (<100 nm, Sigma Aldrich) or titanium dioxide (∼21 nm, Sigma Aldrich) nanoparticles have been calcined at 500 °C for 4 h (ramp of 2 °C min^{-1}) in a constant flow (1 L min^{-1}) of synthetic air. High purity (99.999%) gold (III) chloride hydrate (Sigma Aldrich) has been used as a gold precursor. Urea has been purchased from Sigma Aldrich and stored at ambient temperature. In a typical experiment, 1 g of commercial TiO$_2$ or ZnO nanoparticles have been dispersed in distilled water using ultrasound treatment (45 kHz, 10 min) and heated up to 80 °C. Then, an aqueous solution of gold precursor (24 mg, 1% wt. Au) and urea (300 mg) have been prepared in separate flasks. These reagents have been added simultaneously to the reactor containing the suspension of the metal oxide. The total volume of distilled water is 100 mL. The mixture has been stirred at 80 °C for 16 h and the reactor has been protected against light with an aluminum foil. The obtained creamy precipitate has been washed with distilled water to remove chlorine ions, dried in a vacuum desiccator overnight and reduced under constant flow (1 L min^{-1}) of hydrogen at 300 °C for 2 h (ramp of 2 °C min^{-1}). The obtained powders exhibit a purple color.

2.2. Catalysts characterization

A JEOL JSM 2100F High Resolution Transmission Electron Microscope operating at 200 kV with 2.3 Å resolution has been used for HRTEM imaging. The powder-diffraction patterns have been obtained using SEIFERT XRD 3000 TT X-Ray Diffractometer with Cu-Kα radiation, fitted with a diffracted-beam graphite monochromator. The data have been collected in the 2θ configuration between 20 and 80°. The specific surface area has been determined by the Brunauer-Emmett-Teller (BET) method at 77 K using an ASAP 2020 Physisorption Analyzer. Chemical analyses of Au, Cl, O, and metal cation of the support (Ti or Zn) have been performed by Inductively Coupled Plasma Atom Emission Spectroscopy at the CNRS Center of Chemical Analysis (Vernaison, France). The

amount of Au (wt.%) is expressed in gram of Au per gram of sample: wt.%Au = [m_{Au}/(m_{Au} + $m_{support}$)] × 100.

2.3. Gas test set-up

Five commercial SnO$_2$-based gas sensors (Microchemical Sensors, Switzerland) have been used for the sensing tests. The sensors temperature has been controlled by a constant-voltage supply of 2.5 V (temperature on the sensitive layer ∼480 °C). The conductivity measurements of the sensitive layers have been carried out at ambient temperature and 40% RH, within a test chamber with a gas flow rate of 1 L min^{-1}. The efficiency of the catalytic filter is evaluated comparing the normalized sensors response in the presence or not of the catalytic filter. It is known that nanocomposites are able to catalyze CO to CO$_2$ at room temperature with AuNPs <5 nm and that SnO$_2$ gas sensors are not sensitive to CO$_2$. Therefore, in the presence of Au/MOx (M = Zn, Ti) the lowering of the normalized response to a known CO amount will indicate that CO gas has been removed in presence of the nanocomposites before reaching the SnO$_2$ sensors. The normalized sensors response (R_n) is calculated from the following formula:

$$R_n(\%) = 100 \times (R_{air} - R_{gas})/R_{air},$$

where R_{air} corresponds to the sensor resistance in synthetic air and R_{gas} corresponds to the sensor resistance in reducing gas mixture. Two settings have been investigated:

1) The filter is placed upstream the measurement cell, directly in the gas supply tube,

The size of the grains of the catalytic filter powder is of great importance in order to ensure homogeneous diffusion of the gas. Therefore, all samples (*i.e.* 350 mg of the catalyst) have been grinded following the same procedure before being placed in a quartz tube (d = 15 mm) in the gas line, so that the gas has to pass through the catalytic layer before reaching the measurement cell (Fig. 1a).

2) The filter is placed above each sensor (integrated sensing device)

The catalytic filter (50 mg), prepared as described above, have been placed in a plastic cap connected above the sensor. The gas has therefore to pass through the catalytic layer before reaching the sensing layer (Fig. 1b).

3. Results and discussion

3.1. Catalysts characterization

Metal oxide supported gold nanoparticles have been prepared by the method of deposition-precipitation with urea (DPU) on two different commercial nanopowders: ZnO and TiO$_2$. DPU consists in hydrolysis of urea leading to a progressive release of hydroxide ions in solutions containing solid metal oxide and gold precursor [24,25]. The increase of pH leads to the adsorption of the gold precursor molecules on the metal oxide surface. This adsorption depends on the value of the isoelectric point of the metal oxide. Note that the deposition of gold nanoparticles does not seem to be effective on metal oxides with an isoelectric point below 5.0 or on activated carbon [26,27]. The values of the isoelectric points are 4.7-6.2 and 8.7-10.3 for TiO$_2$ and ZnO, respectively [28]. Therefore, metal oxides chosen for this study are appropriate for the preparation of catalytic filters by DPU.

The diffraction patterns exhibit only hexagonal zincite phase (space group $P6_3mc$, JCPDS 26-1451) or 70% anatase, 30% rutile phase (space group $I4_1$/amd, P4/mnm, JCPDS 75-2545, 77-0442) for ZnO or TiO$_2$ supports, respectively (Fig. 2). Average crystallite size of the metal oxide supports (FWHM) have been calculated by Debye-Sherrer relation. The calcination of metal oxides leads to an increase