Nanocomposites SnO$_2$/Fe$_2$O$_3$: Sensor and catalytic properties

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Abstract

Nanocomposites SnO$_2$/Fe$_2$O$_3$ have been obtained in whole concentration range (0–100 mol% Fe$_2$O$_3$) using wet chemical synthesis. The gas sensor properties of nanocomposites towards CO (40–150 ppm), ethanol (10–200 ppm), H$_2$S (2–10 ppm) and NO$_2$ (50 ppb–10 ppm) have been studied by conductance measurements in temperature range 150–450 °C. Balancing the SnO$_2$/Fe$_2$O$_3$ molar ratio sensors performances can be tailored to obtain materials suitable for different applications. High responses towards ethanol together with low humidity effects have been observed for samples with a high Fe$_2$O$_3$ content ($x > 70$ mol%). Acidic and redox properties of the samples were characterized by NH$_3$-TPD and H$_2$-TPR, respectively. Catalytic properties of nanocomposites were studied in ethanol oxidation using continuous-flow catalytic system. It is demonstrated that increase of Fe$_2$O$_3$ content reduces the amount of surface acid sites and enhances the oxidizing capability of nanocomposites in ethanol oxidation.
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1. Introduction

Complex oxide nanocrystalline systems (nanocomposites) based on semiconductor oxide (SnO$_2$) and catalyst (Fe$_2$O$_3$, MoO$_3$ and V$_2$O$_5$) are of great interest for creation of selective semiconductor gas sensors. Second component can form a solid solution in the bulk [1–5] or a monolayer on the surface of major phase crystallites [6–9], or an own phase. Depending on the molar ratio of components, each system differs in nanostructure, redox properties and acidity/basicity of the surface. These parameters determine sensor and catalytic properties of nanocrystalline oxide systems. In present work, we studied the sensor properties of SnO$_2$/Fe$_2$O$_3$ nanocomposites with different component distribution toward CO, H$_2$S, NO$_2$, and ethanol. The effect of molar SnO$_2$/Fe$_2$O$_3$ ratio on sensor properties of nanocomposites was investigated by various physical and physico-chemical methods. The materials prepared were also tested as catalysts in ethanol oxidation.

2. Experimental

SnO$_2$-based samples were prepared by conventional hydrolysis of SnCl$_4$ followed by impregnation of dried resulting gel by Fe(NO$_3$)$_3$ [1]. Fe$_2$O$_3$-based samples were elaborated by hydroxides co-precipitation from solution containing SnCl$_4$ and Fe(NO$_3$)$_3$ with subsequent thermal annealing. The hydrolysis was realized using an aqueous solution of hydrazine monohydrate, N$_2$H$_4$·H$_2$O [2,7]. Throughout this paper, compositions will be given as (Fe$_2$O$_3$)$_x$(SnO$_2$)$_{1-x}$ with the ratio [Fe]/([Fe] + [Sn]) equal to $2x/(x + 1)$.

The composition and nanostructure of the powders have been investigated by EDX spectroscopy, XRD, TEM, Raman spectroscopy, BET measurements [1,7] and Mössbauer spectroscopy [2]. It was demonstrated that depending on the molar ratio of components and annealing temperature nanocomposites SnO$_2$/Fe$_2$O$_3$ exhibit SnO$_2$-based single phase system, or three-phase system composed by SnO$_2$-, Fe$_3$O$_4$- and Fe$_2$O$_3$-based solid solutions, or two-phase system of SnO$_2$- and Fe$_2$O$_3$-based solid solutions, or Fe$_2$O$_3$-based single phase system [1]. Samples presented in this study differ in the distribution of minor component between the bulk and surface of the grains of major phase. Sample characteristics are summarized in Table 1.

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Table 1
Sample characteristics

x in $(Fe_2O_3)_x(SnO_2)_{1-x}$ (EDX)	T_{anneal} (°C)	Phases (XRD)	Crystallite size (nm) (XRD, TEM)	Surface area (BET)	Mutual distribution of components	Tests performed	
						Sensor properties	Catalytic properties
1	300	α-Fe_2O_3	16	75	Pure component [1]	+	+
0.975	500	α-Fe_2O_3	26	45	Sn^{4+} substitutes Fe^{3+} in metal positions in Fe_2O_3 crystal structure [3]	+	
0.72	300	α-Fe_2O_3	16	125	Sn^{4+} is distributed between bulk and surface of Fe_2O_3 grains with formation of SnO_2-like small islands strongly bonded to the surface Fe^{3+} cations. [1,2]	+	+
0.04	300	SnO_2	4	120	Fe^{3+} substitutes Sn^{4+} in metal positions in SnO_2 crystal structure with the growth of Fe^{3+} concentration (segregation) in near surface region [1]	+	+
0.015	300	SnO_2	4	150	Fe^{3+} substitutes Sn^{4+} in metal positions in SnO_2 crystal structure [2]	+	
0	300	SnO_2	4	120	Pure component [1]	+	+

Sensitive materials have been deposited on alumina substrates provided by interdigitated Pt contacts on the front side and a Pt meander as heater on the backside. Measurements have been carried out by flow through technique in a temperature-stabilized sealed chamber (volume of 1 l) at 20 °C under controlled humidity, working with a constant flux of 0.3 slm. Gas mixtures were generated by certified dry air bottles with diluted target gases concentrations and a humidity system.

DC volt-amperometric measurements ($U = 1$ V) have been carried out to monitor samples' electrical conductivity (G) during exposure to CO, ethanol, H_2S and NO_2. Responses have been calculated as $\Delta G/G$ for reducing gases (CO, ethanol, H_2S) and as $\Delta R/R$ for oxidising gas (NO_2).

The catalytic activity of SnO_2/Fe_2O_3 nanocomposites in ethanol oxidation was studied at atmospheric pressure in a continuous-flow quartz microreactor. The powdered materials were pelletized under 50 MPa, crushed into 0.5–1.0 mm particles and placed into the reactor between two layers of quartz particles. Prior to catalytic experiment the samples were pretreated at 400 °C in a flow of dry air for 6 h. The reactor was heated with a temperature controlled tubular furnace. Ethanol was delivered by passing the air flow of 60 ml/min through a saturator with ethanol at 0 °C. The weight hourly space velocity (WHSV) was 1 g/(g h). The reaction temperature was varied from 200 to 400 °C.

The identification of reaction products was carried out by chromato-mass spectroscopy, using Hewlett–Packard 5890 gas chromatograph with a HP-FFIP column and MS detector HP 5971A. The O-containing reaction products were analyzed on a computer-interfaced M-3700 gas chromatograph equiped by a 6-m Carbowax column; light hydrocarbons, CO and CO_2 were analyzed on a CHROM-5 chromatograph with 4-m Porapack-Q column.

Temperature-programmed reduction with H_2 (H_2-TPR) and adsorption of NH_3 for temperature-programmed desorption experiments (NH_3-TPD) were performed using H_2/N_2 (5%) and NH_3:N_2 = 1:1 gas mixtures, respectively. Before the exper-

iments, the samples were pretreated for 2 h at 400 °C in a flow of helium. NH_3-TPD was carried out in helium flow after purging the sample at 50 °C during 60 min to decrease the amount of physisorbed ammonia. The temperature was increased with a rate of 8 °C/min up to 800 °C.

3. Results and discussion

3.1. Sensor properties

Responses towards CO as function of working temperature are plotted in Fig. 1. Curves relative to samples with high Fe_2O_3 content ($x = 0.975$ and $x = 0.72$) have similar shapes. Response intensities are maximized at the working temperature of 250 °C, with intensity increasing with decreasing the iron oxide fraction. Further lowering this fraction down to $x = 0.15$ enhance such a behavior and increase the working temperature at which response intensity is maximized.
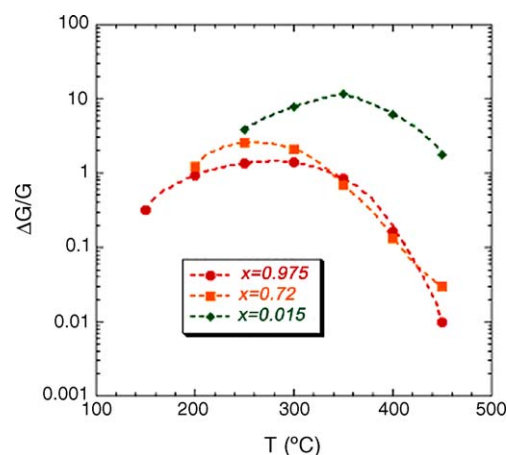

Fig. 1. Responses towards CO (150 ppm) as a function of the working temperature, RH = 30%.