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Eni Carbon Silicates: Innovative Hybrid Materials for Room-Temperature Gas Sensing †

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Abstract: The purpose of this work was to satisfy both materials and technological sciences, on the one hand implementing innovative hybrid materials referred to as ECS (Eni Carbon Silicate) in gas sensors manufacturing, and on the other hand verifying their possible operation at room temperature as a technological progress. The ECS-14 and ECS-13 phases were employed as functional materials for films deposited by drop coating onto alumina substrates. Room-temperature gas tests were performed to study their potential sensing properties. In humidity conditions, the ECS-14 based sensor showed outstanding performance and a complete calibration vs. moisture concentration was obtained.

Keywords: microporous hybrid materials; humidity gas sensor; room temperature

1. Introduction

A sensor is a device that detects events or changes in quantities and provides a corresponding output, generally as an electrical or optical signal. Sensors are used in everyday objects for innumerable applications; from common uses such as temperature, pressure or flow monitoring to particular purposes such as DNA selection. Nowadays, in order to satisfy market demands, materials and devices for sensors production must be increasingly miniaturized, eco-friendly, energetically efficient, reliably multitasking, and low-cost. Then, the research in material and technological sciences has gained a huge development to reach the expectations [1,2]. Moving towards these requirements, hybrid nanomaterials are a fundamental alternative with respect to well-established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. The interest in hybrid materials composed of organic and inorganic units arises from the possibility of combining the advantages of both components, that is, mechanical, structural, and hydrothermal stability of the inorganic compound and the flexibility and functionality of the organic one, favorable for catalyzing consecutive or cascade reactions [3]. New crystalline phases ECSs have every silicon involved in one Si-C covalent bond, and they are obtained by using different bis-silylated organic precursors as silica source, without surfactant agent and $NaAlO_2$ is the source of aluminum. The presence of aluminum plays a relevant role favoring the crystallization of ECS's. The novelty of these materials concerns their structures, crystalline aluminosilicate scaffoldings with long-range 3D order, which distinguish them from the previously reported amorphous and ''crystallike'' silica-based PMOs (Periodic Mesoporous Organosilicas). This is the result of a high-refined development of hybrids synthesis started from zeolites, since hybrids add variable chemical modification to the repertoire of zeolites, which are well established as heterogeneous catalysts, ion exchangers, and molecular sieves with many different pore architectures. These new materials could have very interesting properties, allowing the preparation of new functional active sites with tunable geometrical and chemical properties [4].

Regarding the research in technological science nowadays, solid-state devices have evolved rapidly improving the quality and decreasing the processing and operating costs. From this point of view, metal-oxide gas sensors represent an achievement thanks to their attractive features as discrete reliability and repeatability of the measurement, very high sensitivity even at low gas concentration, and low costs of manufacturing and small dimensions that allow a suitable integration for different uses making gas sensors fundamental in several fields. Despite this, sensors based on metal oxides provide high power consumption, which supports chemical reaction at the surface, and very low response at room temperature characterized by an irreversible behavior. Room-temperature operation is an extremely valuable goal in gas sensing research, due to intrinsic safety of sensors working in harsh or industrial environment. Moreover, it is interesting to reduce power consumption and consequently the size of associated electronics. In recent years, photo-activation mechanism has represented a precious alternative to achieve room temperature gas sensing [5,6].

The purpose of this work was to satisfy both sciences, on the one hand implementing innovative hybrid materials referred to as ECS (Eni Carbon Silicate) in gas sensors manufacturing, and on the other hand verifying their possible operation at room temperature as a technological progress.

2. Materials and Methods

Among ECS phases, the crystalline state and the hexagonal microplatelet-like morphology characteristic of ECS-14 features favorable properties to obtain continuous and uniform films [7]. ECS-14 consists of organic-inorganic layers bonded together by sodium ions and crossed by linear channels, an ideal condition for gaseous analytes diffusion. In addition, ECS-13 shows a crystalline state and a square-shape-platelet morphology. It is formed by composite organic-inorganic layers, which stack in the same manner as found in ECS-14 [8].

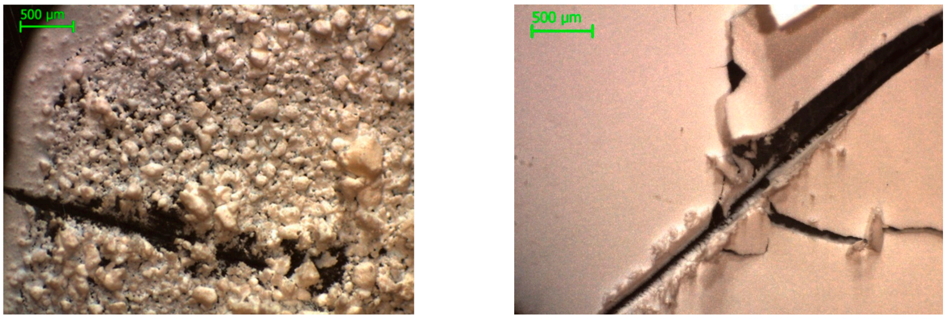
The research activity was divided in two parts: development of preliminary studies about the role of solvents and investigation on the suitability of ECS powders as suspensions for resulting film depositions. In the second part, ECSs were used as functional material in screen-printable compositions, named ECS-14P and ECS-13P. The samples were deposited by drop coating on glass and silicon substrates for morphological (optical and SEM microscopy), structural (XRD), and thermal (TG-DTA) characterizations, and onto alumina substrates with gold interdigitated electrodes for electrical characterization (gas tests). In order to assess any possible employment of this material as a sensing device, the film were exposed to several analytes, i.e., methane, acetaldehyde, ammonia, acetone, toluene, ethanol, benzene and humidity. The gas measurements were carried out in a suitable test chamber with controlled atmosphere and the sensors response was calculates as normalized conductance variation $R = (G_{gas} - G_{air})/G_{air}$. Both the sensing films processing and the gas measurements were performed at room temperature [9].

3. Results and Discussion

3.1. Solubility Tests and Film Deposition

Firstly, ECS powders were mixed with different solvents, as dispersing medium, to investigate the solubility and the filmability of the material. Several solvents were tested as function of their polarity: water, acetic acid, methanol, ethanol, acetonitrile, acetone, dichloromethane, chloroform, toluene, benzene. Among these solvents, ethanol and acetone showed such effectiveness dispersive/disaggregating properties on the ECS film deposited by drop-coating. In particular, ethanol showed the ability to give continuity to the film, whereas acetone revealed a significant disaggregating capacity.

The ECS films, deposited starting from suspensions of ethanol or acetone, were not sufficiently compact to obtain repeatable layers for sensing devices. Then in a second step of the research, ECS powders were mixed with organic vehicles as dispersing medium, generally used in the sensing field for the production of screen-printing pastes based on oxide semiconductors. In this way, ECS powders were used as functional material in the preparation of a screen-printable paste. The suspensions were treated with two cycles of ultrasounds (each of one hour, 300 W power at 50 °C) and deposited by drop-coating [7]. Figure 1a shows a not uniform and continuous ECS-13P film with significant agglomerates. Then, it was decided to add ethanol for its dispersive properties and to use magnetic stirring treatment in order to enhance the disaggregation of possible agglomerates. It can be observed that the addition of ethanol (Figure 1b) gave a greater continuity to the film than the formulation without ethanol. Moreover, the introduction of magnetic agitation as disaggregating treatment had conferred greater uniformity to the film considerably reducing the quantity and size of the agglomerates.



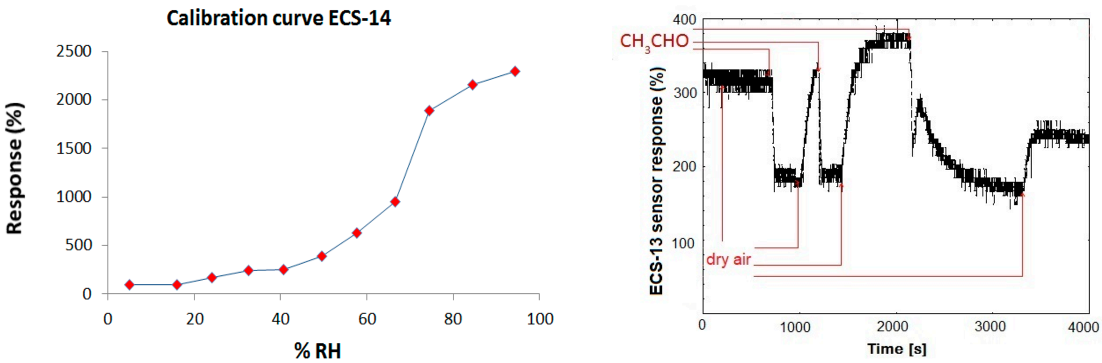
(**a**) (**b**)

Figure 1. ECS-13P film without (**a**) and with (**b**) ethanol addition and magnetic stirring treatments. Images obtained by a stero-optical microscope Leica EZ4.

3.2. Study of Gas Sensing Properties

Significant results were obtained in presence of humidity, for which ECS-14P film showed a high selectivity at room temperature with response and recovery times extremely lower than those of commercial humidity sensor in the test chamber. A humidity calibration curve of ECS-14 film was achieved (Figure 2a) [10].

Even ECS-13P film showed an electrical activity with a low response to 10 ppm acetaldehyde (Figure 2b). Since the importance of this gas from the health and safety point of view, it will be fundamental to deeply investigate the performance of ECS-13P film in presence of this analyte [9].



(**a**) (**b**)

Figure 2. (**a**) The percentage response of ECS-14P film vs. humidity concentration. (**b**) Dynamic response of ECS-13P film tested with 10 ppm of acetaldehyde (CH_3CHO) in dry conditions.

4. Conclusions

By applying a multiscale characterization approach (Scanning Electron Microscopy, X-ray Diffraction, Thermo-Gravimetric analysis), we demonstrated the stability and functionality of films prepared with ECS powders by simple deposition technique. The electrically active films prepared with ECS powders by simple deposition technique can be employed as functional layers in gas sensors. The devices obtained with the ECS hybrids have the properties of speed, reversibility and selectivity fundamental for a good quality electrical response that makes them competitive with respect to systems currently in use. The technological advantage of room temperature operating and the selectivity are added to the novelty of the application of ECSs as active materials in gas sensing.

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