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Development of a porous layer catalytically activated for improving gas sensors performances

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Abstract

A screen-printed thick film was developed to be overlapped to a gas sensing device for preserving it from contamination and degradation occurring in hostile environments, and also for improving its selectivity to a single pollutant gas when exposed to a complex atmosphere. This protective layer incorporated Al_2O_3 doped with Cs or Ba oxides as a catalyst material for eliminating gaseous interfering species, precisely CO_2, to improve sensor response to CO. The best performances were obtained by depositing two, successive layers: the lower one, made of an alumina sol with a dispersed commercial α-alumina powder, just plays the role of protecting the sensitive material and electrodes from degradation, while the upper layer was obtained by the deposition of a screen-printable ink made of doped-alumina powders and is able to selectively adsorb CO_2, just allowing CO to interact at the sensing material surface.

Keywords: A. Films; B. Microstructure-final; E. Sensors; Carbon monoxide

1. Introduction

In previous works [1–3], a porous protective layer has been developed by screen-printing for preserving an electrochemical planar gas sensor from contamination and degradation occurring in hostile conditions, such as car exhaust emissions or other gaseous flows from combustion processes. Sensors without protective layers underwent a fast degradation on engine bench where soot could deposit above the electrodes and induce an electrical short circuit [1].

In that case, the protective layer was a highly porous, alumina-based film having a mean thickness of 40 μm screen-printed on the upper surface of the sensing device.

To obtain such protective layer a screen-printable paste was prepared by mixing suitable amounts of a concentrated alumina-based sol obtained by peptization of Al-hydroxide precipitate [1] and a commercial α-alumina powder. Such a film also showed a low catalytic activity for CO_2 adsorption [2]. This behaviour coupled to medium–high specific surface area values offered an interesting perspective for further developments through its catalytic activation for improving the sensor selectivity to a single pollutant gas, when exposed to complex gas mixtures. This paper deals with a further evolution of this protective layer consisting in its catalytic activation by suitable metal oxide catalysts. This activated layer can be properly used to improve the response of semiconducting metal oxides, generally used as sensing materials, but showing a poor selectivity [4,5]. To overcome this problem, for instance, high-temperature gas filters located directly at the surface of the sensing film have been already proposed [4,5] to suppress signals of unwanted gas components like CH_4, C_2H_6, CO and NO in H_2 detection. The action of a gas filter may be two-fold [4,5]:

- to hinder the interfering gas from reaching the detection substrate, but to allow the gas to be detected to reach the sensor surface;
- to transform the gas mixture to be detected into mixture which favours the detectability of the target gas.

However, there is no evidence in the literature of a catalytic, protective film, able to improve the sensor response to CO in a CO/CO_2 mixture.

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Basic metal oxides added to alumina can effectively adsorb CO_2 from an N_2-containing gaseous mixture at elevated temperatures [6]. Modifiers examined were the oxides of alkali metals (Na, K, Rb, Cs), alkaline earth metals (Mg, Ca, Sr, Ba) and some rare earth metals (La, Ce, Nd, Pr).

In the present study, modified alumina catalysts based on K, Cs, Mg, Ba, La and Zn oxides were sol–gel prepared and tested for selectively adsorbing CO_2 from CO/CO_2 mixtures. Particularly, Al_2O_3 doped with Cs and Ba oxides have presented very promising results for the proposed application.

2. Materials and methods

To develop the catalytically activated, protective layer, firstly powdered materials have been prepared and characterised for a pre-screening and selection.

Cs_2O- and BaO-modified aluminas were sol–gel prepared starting from aluminium tri-*sec*-butoxide in ethanol, followed by the addition of the oxide precursor (oxalate or acetate) dissolved in water, and eventually complexing (e.g., ethyl acetoacetate) and/or activating agents (e.g., HCl or HNO_3) to control the rate of the hydrolysis and condensation reactions. After gelation and vacuum removal of the solvent, the materials were dried at 100 °C and finally calcined up to 700 and 900 °C.

The specific surface areas of the calcined samples were measured by chemisorption of N_2 from a flowing mixture 30% N_2–70% He at 77 K (BET "single point" method). Then, in order to study the activity and selectivity of the modified aluminas, the following characterization tests were performed: (i) pulse chemisorption of pure CO_2 up to saturation at 300 °C in a static apparatus (Micromeritics Pulse Chemisorb 2705) and thermal desorption (TPD) at 10 °C min^{-1} up to 700 or 900 °C under flowing helium (the cycle was repeated two to three times); (ii) chemisorption of CO_2 up to saturation at 300 °C in a flowing apparatus (plug flow microreactor) from $He/CO/CO_2$ and/or $N_2/O_2/CO/CO_2$ mixtures, followed by desorption under flowing helium up to 450 °C (the cycle was repeated up to 10 times).

Every thick film screen-printed has been treated, in air, with the same thermal cycle: an initial heating ramp at 5 °C min^{-1} up to 200 °C, followed by a heating at 1 °C min^{-1} ramp up to 700 °C with a soaking time of 1 h and a cooling step at 5 °C min^{-1} to 30 °C.

SEM images and EDS analyses were performed by a scanning electron microscope (SEM) Hitachi S2300.

3. Experimental

3.1. Post-impregnation of an alumina-based porous, protective film

To prepare the upper catalytically activated film, the first and the simplest option was to perform a post-impregnation of the already developed porous, protective layer [1], since it was partially made of transition alumina, then it was able to act as a suitable catalyst support [3]. So, a preliminary characterisation in terms of CO_2 adsorption was performed, before any further catalytic activation. To compare its behaviour to those of the doped-alumina powders, the protective layer was reduced in powder and calcined at 700 °C for 1 h. This material was made of transition alumina and commercial α-Al_2O_3 (Friatec AG No. 59257, Degussa, Germany) obtained by mixing a concentrated aluminium hydroxide sol to the α-Al_2O_3 powder in a weight ratio of 4:1 (sample P1) [2]. As a comparison, pure transition alumina powder was also obtained by heat treating the pure sol at 700 °C for 1 h (P2).

Table 1
Specific surface areas of the powders heat treated at 700 °C

	Samples	
	P1	P2
Specific surface area ($m^2\ g^{-1}$)	1.8	152

Table 2
CO/CO_2 chemisorption results (mmol g^{-1}) of P1 and P2 samples

Chemisorbed gas	Samples	
	P1	P2
CO at 150 °C	0	0
CO at 500 °C	0	0
CO_2 at 150 °C	1.6×10^{-3}	5.4×10^{-3}
CO_2 at 500 °C	1.8×10^{-3}	8.0×10^{-4}

Specific surface area measurements have been performed on both samples (Table 1) and the relevant difference in S.S.A. is imputable to the different amount in transition alumina in these two materials.

The results of pulse chemisorption of pure CO_2, expressed in mmol of gas at saturation point for 1 g of sample, are resumed in Table 2.

The powders simply obtained by the previously developed protective layer showed a very low catalytic activity for CO_2 adsorption. For this reason, it was decided to improve their catalytic activity for CO_2 adsorption by performing a post-impregnation of the porous, protective layer, by using a barium oxide precursor solution, in order to homogeneously disperse a better CO_2 adsorbent on the transition alumina-based layer. P1 and P2 samples were soaked in a barium nitrate aqueous solution. Two grams of both samples soaked in 20 ml of a saturated solution of this salt, under mechanical stirring, at 80 °C for 1 h and then at 20 °C for 6 h. Finally, powders were filtrated and dried overnight. These materials are labelled as P1/BaO and P2/BaO, respectively.

Table 3
Specific surface areas of doped aluminas

Samples	Specific surface area ($m^2\ g^{-1}$)	
	Calcination at 700 °C	Calcination at 900 °C
Transition alumina (P2)	205	147
Al_2O_3/Cs_2O (P3)	266	195
Al_2O_3/BaO (P4)	215	158

Table 4
CO/CO_2 chemisorption results (mmol g^{-1}) on impregnated powders P1 and P2 and on doped aluminas P3 and P4

Chemisorbed gas	Samples					
	P1/BaO	P2/BaO	P3/700	P3/900	P4/700	P4/900
CO at 150 °C	0	9.8×10^{-4}	0	5.6×10^{-4}	0	0
CO at 500 °C	4.1×10^{-4}	3.2×10^{-4}	4.0×10^{-2}	2.6×10^{-3}	0	1.9×10^{-3}
CO_2 at 150 °C	0	2.9×10^{-2}	1.9×10^{-1}	1.9×10^{-1}	4.5×10^{-2}	1.5×10^{-1}
CO_2 at 500 °C	2.7×10^{-3}	3.3×10^{-3}	2.15×10^{-2}	1.38×10^{-1}	5.3×10^{-3}	1.79×10^{-2}

Also in this case, the preliminary characterisation was performed on powdered materials for an easy comparison with the doped aluminas results.

Specific surface area measurements were performed on pure transition alumina (P2) and on modified aluminas prepared from Cs oxalate (P3) and from Ba acetate (P4) precursors, heat treated at 700 and 900 °C, for 1 h, prior N_2 adsorption measurements (Table 3). The determined values were rather high after thermal treatment.

Chemisorption analyses were also then performed on these samples (Table 4).

The results showed that the catalytic activity of P1/BaO and P2/BaO was rather low: CO/CO_2 chemisorptions on these samples were limited, even if a preferred CO_2 adsorption was observed.

The direct impregnation of the powders P1 and P2 did not allow the preparation of an effective catalytic layer. CO_2 retention was in most of the cases higher in P3 sample, respect to P4 and respect to CO, whatever the temperature treatment. Therefore, it was decided to incorporate the more active powders (P3 and P4) directly in the thick layer composition.

3.2. Catalytically activated thick film development

Since the deposition of the porous protective thick layer is performed by screen-printing a suitable paste through screen openings of 45 μm, it was firstly necessary to check the particle size distribution of P3 and P4 powders to avoid any sieving effect of the powder on the screen. Particle size distribution of the powders P3 and P4 calcined at 700 °C were affected by large agglomerates (Table 5) and a 2 h milling, in a planetary mill in agate jars with agate spheres and ethanol, was necessary to make them suitable for screen-printing process. The particle size distributions were measured by means of a Fritsch Analysette 22 compact laser granulometer, after dispersion in ethanol and 10 min ultrasonication.

Table 5
Diameters at 10, 50 and 90 % cumulative distribution of the doped aluminas (P3 and P4) treated at 700 °C before and after milling

Samples	Diameter (μm)		
	$Ø_{10}$	$Ø_{50}$	$Ø_{90}$
P3	4.78	19.50	64.68
P4	4.20	17.96	61.95
P3 2 h milling	2.55	6.42	13.26
P4 2 h milling	2.28	4.96	10.87

Thermogravimetric and differential thermal analysis (TG-DTA) were performed on a Netzsch STA 409 apparatus with a heating rate of 10 °C min^{-1} until 900 °C (Fig. 1) and the mass loss was negligible at temperatures over 700 °C. Then, 700 °C was the temperature chosen for powders calcinations prior to ink preparation, in order to limit the shrinkage during thermal treatment of the films, which must be performed to induce adhesion to the substrate. The different peaks on DTA curves (Fig. 1) were associated to the thermal decomposition of the precursor salts, Cs oxalate and Ba acetate, respectively.

A screen-printable ink was prepared by dispersing the powder (2 g) in 1.5 ml of an organic solvent (Emflow 227, Emca-Remex products, England) added with 0.0625 g of an organic binder (poly vinyl butyral-co-vinyl alcohol-co-vinyl acetate, PVB, Aldrich, Germany). This formulation will be labelled from now on as ‘‘traditional ink’’. After deposition on α-alumina plates for

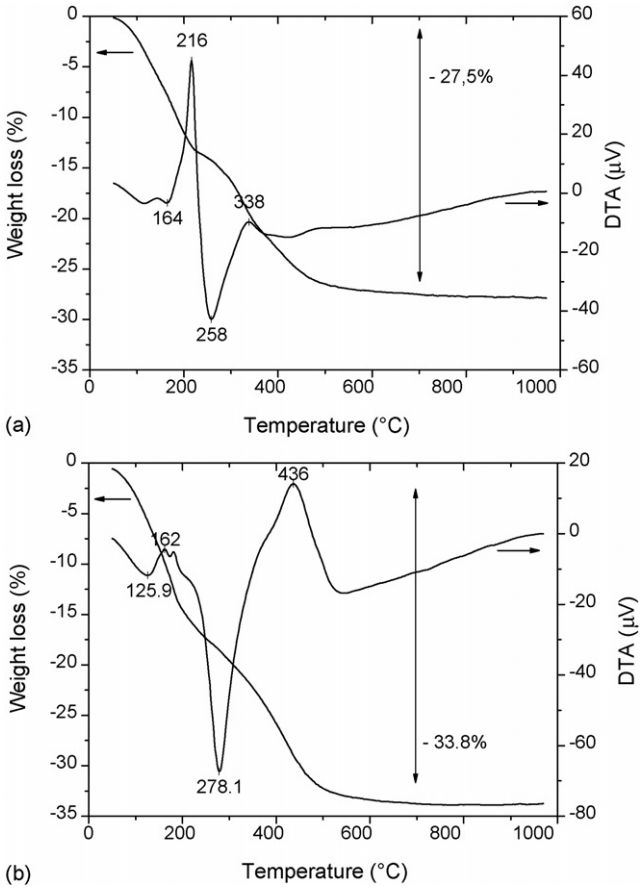

Fig. 1. TG-DTA measurements on: (a) P3 and (b) P4 powders.

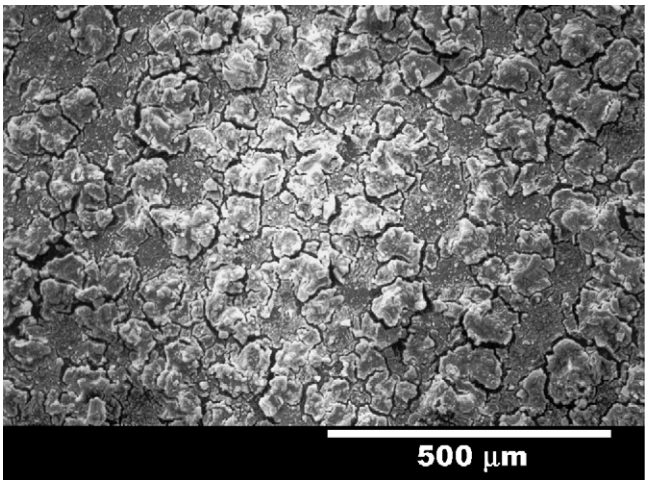

Fig. 2. SEM image of the screen-printed film treated at 700 °C for 1 h, made from P4 dispersed in the concentrated sol.

electronics, the films were fired at 700 °C for 1 h, but scotch tests on fired thick films revealed a poor adhesion.

To improve adhesion, the alumina-based, concentrated sol, already described [2,3], was used as a dispersing medium for the active powders P3 and P4. 0.2 g of solids was then mixed to 3 ml of sol to achieve a suitable viscosity for screen-printing. The thick films were fired for 1 h at 700 °C and their adhesion onto the substrates was once again poor, while SEM image (Fig. 2) showed a diffuse cracking on their surface. This crack appearance is a consequence of the limited load in P3 or P4 powder added to the sol for reaching an appropriate rheological behaviour for screen-printing. The limited amount of the powder added to the sol is therefore not able to contrast the shrinkage induced in the film by the dehydration of the colloidal dispersant during heating.

3.3. Double layer development

To avoid the above drawbacks, the following development step consisted in the overlapping of two thick layers. The lower one was the already developed thick layer made of ink prepared by mixing a commercial α-Al_2O_3 powder dispersed in the concentrated alumina sol; the upper layer was made of a screen-printed traditional ink containing one of the above doped aluminas (P3 or P4). In this case, the traditional ink was prepared by mixing 1 g of catalytic powder to 1.35 ml of Emflow and 0.06 g of PVB. The two layers were overlapped at the green state. Finally, they were fired at 700 °C for 1 h. In this case, the adhesion was significantly improved, but SEM observations still showed the presence of diffused cracks on the surface of the catalytic layers.

In order to reduce film cracking, a new formulation of the traditional ink was tested, by adding also the powder of the metal oxide responsible for the catalytic activity. In the case of Ba, a pure BaO powder (after thermal decomposition of Carlo Erba barium nitrate at 400 °C) was milled in a planetary mill (in agate jars with agate spheres and ethanol) and added in various amounts, precisely P4/BaO with weight ratios 1:1, 1:1.5 and 1:2. Double layers, as described above, were screen-printed and

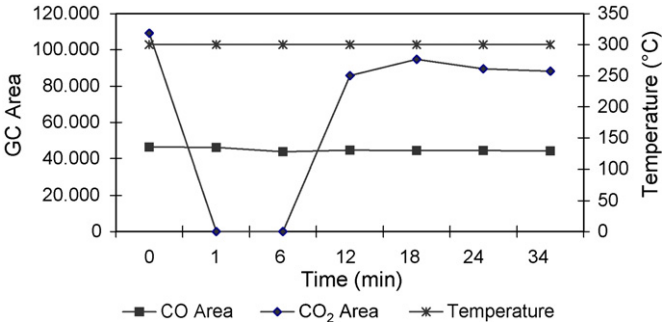

Fig. 3. Chemisorption results of P3 in function of time (fifth cycle).

calcined. Also in this case cracking was present after firing, but in a very limited extent on the layers prepared by using the weight ratios of 1:1 and 1:1.5.

Since by chemisorption analyses, performed in a micro-reactor at 300 °C under 50 ml min^{-1} of flowing 0.1/1/98.9 CO/CO_2/He mixture (Fig. 3), Cs_2O-doped alumina showed the best catalytic effect in selectively reducing CO_2 amount by adsorption, the set up of the porous, protective and catalytically activated layer, was performed by using P3 powders.

For definitively avoiding crack formation, the formulation of the traditional ink was changed once again by replacing the catalytic oxide powder by a commercial α-alumina powder (Friatec).

Then, the new screen-printed double layers were made of an upper film made of a traditional ink prepared with P3 powder mixed with Friatec alumina, by using two different weight ratios of 1:1 and 1:1.5. For preparing this ink, the commercial powder was milled for 7 h. From the granulometric data, the α-alumina powder is finer than P3 (Fig. 4) in order to fill up the voids among P3 grains and to limit the global shrinkage.

Once again, the adhesion between the layers was good and cracking (Fig. 5(a)) was considerably reduced and limited only to the surface of the upper layer, as it clearly appears by the observation on the double layer cross-section (Fig. 5(b)). The best result was achieved by using the ink made of P3/Friatec Al_2O_3 in a weight ratio of 1:1.5.

Finally, to improve catalyst amount, in this upper layer, the commercial α-Al_2O_3 powder was replaced by using a P3 powder pre-treated at 900 °C. Also this powder was milled and after a 2 h milling the mean diameter was 2.52 μm, that is a

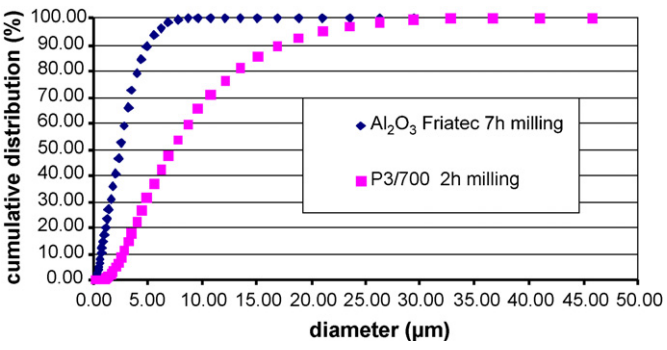

Fig. 4. Particle size distribution for P3 and Al_2O_3 Friatec powders.

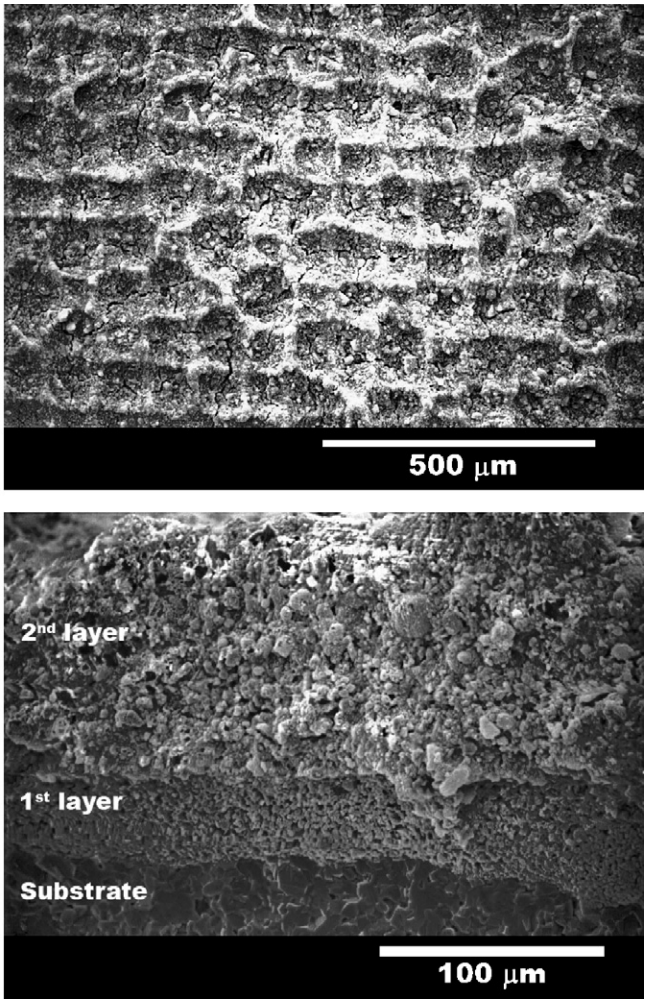

Fig. 5. (a and b) SEM images of double layer water-based Al_2O_3 sol/P3/Al_2O_3 Friatec 1:1.5, treated at 700 °C for 1 h.

mean value very close to that presented by the ground α-Al_2O_3 powder in order to obtain the same filling effect.

After heat treatment the layers presented a cracking equivalent to that of the layer containing Al_2O_3 and adhesion was good. The two P3 powders were mixed in a weight ratio of 1:1 and used to prepare a traditional ink by mixing 2 g of catalytic powder to 2.7 ml of Emflow and 0.12 g of PVB.

The thickness of each layer was about 40 μm.

4. Conclusions

The feasibility of a planar porous protective layer able to improve CO sensors performances in presence of CO_2 has been demonstrated. The produced thick films showed a good adhesion to the substrate and presented limited cracks. The proposed scheme for this sensor protection includes an intermediate layer between the sensing materials and electrodes and the catalytic layer in order to prevent direct contact between metallic electrodes and catalyst. The effectiveness of this active barrier onto sensor response has now to be verified. The thickness of the developed catalyst layer was rather limited (40 μm), compared to the film mentioned in ref. [4] (300 μm), but the use of a different screen-printing screen (with a lower mesh number) and the optimisation of the ink viscosity can strongly improve the amount of the catalyst deposited.

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