



Aluminium anodisation for Au-CeO₂/Al₂O₃-Al monoliths preparation

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ABSTRACT

The anodisation of aluminium monoliths was performed in order to generate an alumina layer that ensures a good adherence of the catalysts. In this study, it is demonstrated that the morphology of the produced alumina layer depends on time, temperature, current density and concentration of the selected electrolyte. When anodisation process with the extreme conditions was applied (30 °C, 50 min, 2 A dm⁻² and 2.6 M of sulphuric acid) a significant cracks were obtained and used to fix the subsequent catalytic coatings. The washcoating method was used to cover the monoliths with colloidal solutions of CeO₂ and/or Au-CeO₂ catalysts. The resulting monolithic catalysts were tested in the CO oxidation reaction being 1%Au-CeO₂ containing system the most active. The structured catalyst prepared this way changed neither the textural nor the catalytic properties of the deposited catalytic powders.

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1. Introduction

The gold nanoparticles supported on ceria have been widely investigated in the last few years. Most of these studies have focused on their unusual low temperature CO oxidation activity [1–3]. Moreover this catalytic reaction can be used in applications such as purification of breathing air in closed spaces, safety masks, gas sensors for the detection of trace amounts of CO in air, closed-cycle CO₂ lasers, automotive exhaust treatments, etc. Normally, the catalysts are used in fixed bed catalytic applications, randomly packed by powdered micro-granules or extruded pellets few millimetres in size. During the last decades, there has been a growing interest in catalytic reactor engineering based on structured catalytic beds in different chemical processes, mainly in environmental catalysis and combustion processes [4]. Monolithic catalysts comprise the advantages of a low pressure drop (less than 1/10th of that of the packed-bed reactor), a high catalytic performance per mass unit of active-phase, safer operating conditions and easiest catalyst separation [5].

The most common material for monolithic structures is cordierite – the material which suited well the requirements of automotive industry [6]. The main reasons are its high mechanical strength, high resistance to elevated temperatures and temperature shocks due to its low thermal expansion coefficient [7]. However, under certain circumstances, it is preferable to use metallic substrates since they present a series of comparative advantages with respect to ceramics, i.e., higher mechanical resistance, higher

thermal conductivity and better prospects of achieving high cell densities [8]. Many different metals and alloys have been proposed for the manufacturing of metallic monoliths in the search for mechanical, chemical and thermal stability and availability in thin foils, such as Ni–Cr alloys [9], ferritics steel alloys containing Al [5,10], AISI 304 stainless steel [11] and aluminium [5,12,13]. Nevertheless, the preparation of metallic monoliths has a critical point, the adhesion of the catalytic coating to the metallic substrate. When coating the metallic supports with a catalytic material by washcoating, an intermediate layer of ceramic material is often used for better binding [5].

When the working temperature is not too high, aluminium with its excellent mechanical and thermal properties is an interesting material to prepare the metallic monoliths [5]. Moreover, aluminium can be coated with alumina obtained by anodisation and thus the texture can be controlled by tuning up the anodisation parameters such as time, current density, temperature, electrolyte nature and its concentration [12]. The anodic films are composed of amorphous anodic alumina and contain fine porosity present as channels perpendicular to the surface reaching the alumina–aluminium interface [14–16]. This interface is formed by a barrier layer that separates the pores from the metallic aluminium. The pores are contained in alumina cells that can self-organize to a close-packed arrangement [17,18]. The pore diameter and barrier layer thickness are related to the anodising voltage. The formation of porosity has been attributed to the accelerated dissolution of the anodic alumina at the pore bottom due to the high electric field that exists across the barrier layer [19,20]. In aluminium foams, when the anodisation conditions are extreme, an important cracking of the surface appears with wide and deep cracks that depend on the anodisation parameters [13]. The surface roughness can be

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used subsequently to improve the adhesion of the catalytic coatings promoting its mechanical anchorage.

This work makes a significant contribution to the understanding of the preparation parameters for washcoated anodised aluminium monoliths. The washcoating procedure was selected to incorporate CeO₂ and Au-CeO₂ colloidal solutions of conventional powder catalysts to anodised aluminium monolith. The rational selection of the variables of the anodised process in sulphuric acid are described in order to obtain an alumina layer that ensures an adherent catalytic layer. Finally the prepared monoliths were tested in the catalytic oxidation of CO as a test reaction.

2. Experimental

2.1. Structured supports

The aluminium foils (100 μm thickness, 1002 alloy) were obtained from INASA (Industria Navarra del Aluminio S.A.). The aluminium foils (24 × 3 cm) were cleaned with detergent and water before any use. Acetone was then used to remove the remaining organic impurities, and finally the foils were dried.

Anodisation was carried out in an anodisation polypropylene tank with sulphuric acid. Temperature control of ±0.1 °C was obtained with a cooling PTFE coil connected to an external chiller and an electrical heater connected to a PID temperature controller. The power supply used was an Agilent HP 6692A that can operate between 0–60 V and 0–110 A allowing current or voltage control. A vigorous air bubbling assured the agitation inside the bath. After anodisation, foils were taken out of the electrolytic bath, thoroughly washed with water to take out the acid, and they were dried at 60 °C during 1 h and calcined at 500 °C for 2 h.

In order to study the influence of the variables affecting the anodisation process and therefore the final structural properties of the generated alumina on the aluminium foils surface in sulphuric acid at 2 A dm⁻², the following variable ranges were chosen:

- The anodisation time: 30–50 min.
- The electrolyte concentration: 1.6–2.6 M.
- The electrolyte temperature: 20–30 °C.

Al₂O₃-Al monoliths were prepared by rolling around spindle alternate previously anodised flat and corrugated foils. The final monolith is a cylinder of 3 cm height, 1.6 cm diameter and a cell density of 55 cell/cm².

2.2. Powder catalyst preparation

The CeO₂ support was prepared according to the precipitation method described in the literature [21,22]. The adequate amount of cerium nitrate (Ce(NO₃)₃·6H₂O Alfa Aesar, 99.5%) was dissolved in deionised water at room temperature under stirring. Ammonia solution (25%) was added drop wise into solution in order to obtain a precipitate that was filtered, washed with deionised water and kept overnight at 100 °C in an oven.

The gold containing catalysts were prepared by the deposition-precipitation method [2,3]. The adequate amount of HAuCl₄·3H₂O (Alfa 99.99%) to obtain a gold concentration of 0.1% or 1 wt% in the final catalysts was dissolved in deionised water and the pH of the solution was adjusted to 8.0 by addition of NaOH 0.1 M [21]. Then the CeO₂ colloid at pH 8 was added to the gold dissolution. The mixture was kept under continuous stirring for 5 h at room temperature. The obtained solid was separated from the solution by filtration and washed with deionised water until the disappearance of chloride and Na⁺. Finally the powder catalyst was dried during 1 day in an oven at 100 °C.

2.3. Washcoating

10 wt% colloidal solutions of the different solids were prepared by dispersing the powders in deionised water with the help of an ultrasonic bath (Misonix Sonicator 3000, 50 W) during 4 h at room temperature. The solids content of the colloidal solutions was kept constant at 10 wt% (beyond this value their viscosity increase significantly and the colloid is not suitable for homogeneous coating). The viscosity of the prepared colloidal solutions was around 3 cP. This viscosity was adequate to obtain excellent catalytic coating. As previously reported by Agrafiotis and co-workers [23,24] to obtain homogeneous and adherent coatings, the viscosity must be adjusted: low viscosity values promote good adherence but low loadings were obtained, and high viscosity induces high solid loading but poor adherence. The isoelectric point (IEP) of CeO₂ is at around 7 and therefore a pH 3 will ensure a high potential and then high repulsions between the particles which favours the stability of the dispersion [25].

The washcoating of the monoliths was carried out by dipping them in the colloidal solutions for 1 min and withdrawing at a constant speed of 3 cm/h. Afterward, the monoliths were centrifuged at 400 rpm for 10 min to eliminate the excess colloid, and then dried at 60 °C for 1 h. This washcoating procedure was repeated three times to load ≈100 mg catalyst on the monolith. Finally the monoliths were calcined at 300 °C for 4 h.

2.4. Catalytic activity

The catalytic oxidation of CO was performed in a conventional continuous flow U-shaped glass reactor working at atmospheric pressure. The composition of the inlet and outlet gases was analyzed with a Balzers Omnistar Bentchtop mass spectrometer with capabilities for quantitative analysis. The light-off curves for CO oxidation (300 °C, 5 °C min⁻¹) were obtained with a gas mixture containing 3.4%CO and 21%O₂ balanced by He at a total flow rate of 42 ml min⁻¹. A blank reaction in the absence of the metallic monolith (empty reactor), showed no activity under these conditions. The catalytic devices were pre-activated "in situ" at 300 °C for 60 min in synthetic air. The effect of water on catalytic activity was determined by a second test in which the feed bubbles before entering in the reactor through a water saturator at 25 °C (3%H₂O, v/v).

Catalytic measurements over the powder catalysts were carried out in the same operating conditions and equivalent contact time to the monolithic devices. For that purpose a similar amount of powder catalyst (≈100 mg) was diluted in the glass balls to the volume occupied by the monolithic devices.

2.5. Characterization

X-ray diffraction (XRD) analysis was performed on Siemens Diffractometer D500. Diffraction patterns were recorded using Cu-Kα radiation (λ = 0.15404 nm) over a 20–80° 2θ-range and a position-sensitive detector with 0.05° step size at a scan rate of 1° min⁻¹.

The sample morphology was examined with a scanning electron microscope (SEM) Hitachi S-2700. High resolution SEM micrographs were recorded by FE-SEM (HITACHI S-4800).

The adherence of the scale and catalytic layer to the substrate was evaluated using the ultrasonic method [26]. This consists in the measurement of the weight loss caused by the ultrasound treatment. The monoliths were submitted in an ultrasonic bath (Cole Palmer, 47 kHz and 130 W) for 60 min at room temperature and in acetone solution. After that, the samples were dried and calcined. The weight loss was determined by the difference in the mass of the samples before and after the ultrasonic test. The results are

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