

# Nano-CeO<sub>2</sub> Coating on Aluminum Foam Carriers for Structured Catalysts Preparation

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This paper reports the results of a study on the preparation of structured catalysts by chemical conversion coating. The ceria coating was realized by reacting suitably pre-treated aluminum structures with an oxidizing solution of cerium chloride; the obtained samples were characterized by means of several analytical techniques to evaluate the coverage percentage, the surface morphology and the surface chemical structure. A preliminary screening on the reactivity of the system, to find the better operative conditions, was carried out on square plates in order to realize a suitable plating bath for the preparation of a structured catalyst, made up of aluminium foam carrier. The obtained catalyst was loaded with platinum as active phase and tested in water gas shift reaction for hydrogen production.

## 1. Introduction

The water gas shift reaction plays a crucial role in the hydrogen production process, because it can be considered the first purification step of syngas, as it allows to reduce to less than 0.3 % the percentage of carbon monoxide, extremely harmful for the membranes (Tocci et al., 2006). Therefore, the configuration of the water gas shift reactor has recently been the subject of numerous studies, with the aim of carrying out a process intensification (Palma et al., 2018 c). Among the different alternatives, today structured catalytic reactors, characterized by a structured catalyst, are considered a valuable solution with respect to the packed bed reactors based on different particle shapes such as spheres, cylinders, rings, flat disc pellets or crushed material of a certain sieve fraction (Eigenberger, 2008). Structured catalysts, in fact, present several advantages especially for what concerns transport phenomena (Tronconi, 1997), such as heat (Palma et al., 2015) and mass transfer (Palma et al., 2018 b). Aluminum foam based structured catalysts have been extensively studied as ideal candidates for the water gas shift process intensification (Palma, Pisano, Martino, 2017); the high thermal conductivity of the structured carriers is strategic for the intensification of processes based on exothermic reaction, moreover the structured carriers allow to realize specific geometrical configurations. Furthermore the catalytic formulations play a crucial role in the realization of single stage water gas shift process; noble metals over high reducible supports seem to be the most suitable one for this scope (Palma and Martino, 2017). Structured catalysts are normally obtained by washcoating a carrier (Palma and Martino, 2018) with a primer such as alumina (Visconti, 2012), that makes compatible the active formulation with the inert carrier and allows to increase the surface area of the carrier. Alumina is an excellent primer but unfortunately is not inert towards the most reactions, for example towards water gas shift reaction (Palma et al., 2018 a), moreover, the washcoating procedure is cumbersome and expensive, making the possibility to realize a coating with the lonely active components an extremely attractive topic. In this sense, it could be strategic to realize a ceria-based catalyst by means of a ceria coating on aluminum carriers for the preparation structured catalysts. Many coating techniques are available (Meille, 2006), among them, chemical conversion coating (Sánchez-Amaya et al., 2012) can be considered a simple and effective method to obtain resistant (Wang et al. 2004) and uniform protective layers on metallic surfaces. In this contest, many studies on the resistance of cerium-based conversion layers on aluminum alloys were published (Debalà et al., 2001). Plating aluminum with cerium oxide arises as an alternative to chrome plating, as a response to the toxicity problems (Tang et al., 2011), associated to the use of chrome plating baths. At the beginning of the eighties, Hinton et al. (1984) reported that cerous chloride is able to reduce the corrosion rate of aluminum alloys; since

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then a multitude of works have been published on the set-up of the method, however most of them are based on electrodeposition (Balasubramanian et al., 1999). Anyway, electrodeposition presents a series of disadvantages, such as process costs and non-uniform plating, on the contrary, chemical conversion (Bethencourt et al., 2004) seems to be a simple, inexpensive and easily achievable process. The purpose of this article is to show that it is possible to use an aluminum protection technique (plating with cerium oxide), as a preparation method for structured catalyst employed in the water gas shift reaction. With this aim we report our results on the preparation of structured catalyst obtained by chemical conversion coating of ceria on open cell aluminum foam. The first phase of the work was focused on the set up of the method; a series of preparation parameters were investigated, such as the bath temperature, the reaction time and the pH of the bath. The experiments were carried out on square aluminum plates, to make easy the evaluation of the coating by surface analysis. The second phase of the work was devoted to the preparation of an open cell aluminum foam structured catalyst, and to the evaluation on the performance in water gas shift reaction.

## 2. Experimental

### 2.1. Materials

The aluminum square plates were provided by Officina Elettromeccanica Elena Mormile, aluminum foam was provided by ERG Materials and Aerospace; cerium(III) chloride heptahydrate 99 % ( $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ), hydrogen peroxide 35 %, hydrochloric acid 36.5-38.0 %, nitric acid 70 %, sodium hydroxide and acetone were provided by Sigma-Aldrich, tetrammineplatinum (II) nitrate 99 %, was provided by Strem Chemicals, bidistilled water provided by Titolchimica S.p.A.

### 2.2. Chemical coating procedure and catalyst preparation

The aluminum square plates were previously treated to prepare the surface to the chemical coating procedure. The samples were firstly degreased with acetone, then etched with sodium hydroxide solution (5 wt %) for 1 minute, finally treated with nitric acid solution (35 wt %) for 1 minute. After each treatment the aluminum structure was washed with distilled water and, at the end of the pre-treatments, it was immersed in the solution for the coating deposition (plating bath) (Andreeva et al., 2014).

The plating bath was composed by  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  35 wt % and water, in a weight ratio 1/3/75, acidified with HCl (pH=1-3). The treatment was repeated from 1 to 3 times from 10 minutes to 4 hours, and the resulting structure was dried at 393 K for 2 hours.

The structured catalyst was prepared by applying the previous plating procedure (pH=1, 323 K, 2 cycles of 4 hours), to the aluminum foam (40 PPI, 10-12 % relative density); after each cycle it was dried at 393 K for 2 hours and calcined at 723 K for 3 hours. It was reached a ceria surface loading equal to 47.71 wt %. The resulting plated foam was then loaded with platinum by impregnation with a solution of tetrammineplatinum (II) nitrate, dried at 393 K for 2 hours and calcined at 723 K for 3 hours, to obtain the desired platinum loading (0,12 wt% with respect the weight of the structured catalyst).

### 2.3. Characterization techniques

The B.E.T. specific surface areas measurements were obtained with a Costech Sorptometer 1040 (Costech International). The good coating resistance to mechanical stress was evaluated by ultrasound adherence test with an ultrasonic bath CP104 (EIA S.p.A.). The catalysts were dipped in petroleum ether at 298 K and submitted to ultrasound obtained setting the 60 % of rated power of the equipment, for six cycles of five minutes. The XRD diffractograms were obtained a Brucker D8 Advance, with a Cu K $\alpha$  radiation source (35 kV; 40 mA) in the  $2\theta$  range 20-80 °, (Stp= 737; Stp size=0.0814; t/Stp 0.5 s). The crystallite dimensions were calculated from the diffractograms by applying the Scherrer equation. The coating coverage was checked by means of ARL QUANT'X ED-XRF spectrometer (Thermo Scientific, while the structural features evaluated with Raman spectroscopy by an inVia Raman Microscope (Renishaw), equipped with a 514 nmAr ion laser operating at 25 mW. Samples morphology was observed by a Field Emission Scanning Electron Microscope (FE-SEM, mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany). The  $\text{H}_2$ -TPR experiments were performed, before the activity tests, with a reducing stream of 500 Ncc/min containing 5 vol% of  $\text{H}_2$  in  $\text{N}_2$ , in the temperature range of 300-725 K, an heating rate of 10 K/min.

### 2.4. Activity tests

The activity tests were carried out at atmospheric pressure, in the temperature range of 520-630 K, with a reaction mixture of 4 %  $\text{CO}$ , 20 %  $\text{H}_2\text{O}$  and 76 %  $\text{N}_2$ , in a stainless steel tubular reactor with an internal diameter of 17 mm and 83 mm long, at a WHSV of 125  $\text{g}_{\text{CO}}/\text{g}_{\text{Pt}} \cdot \text{h}^{-1}$ . The reaction product composition on dry

basis was monitored through an ABB system equipped with the non-dispersive infrared analyser Uras 14 for CO, CO<sub>2</sub> and CH<sub>4</sub> and a thermal conductivity detector Caldos 17 for H<sub>2</sub>.

### 3. Results and discussion

#### 3.1. Operating conditions screening

First of all, it was carried out a preliminary screening to find the optimal operating conditions for the coating by a plating bath, by evaluating some critical process parameters, such as pH, time of reaction, number of cycles and bath temperature (see table 1), in terms of CeO<sub>2</sub> weight percentage of the aluminum surface, by mean of XRF analysis. For this screening, aluminum square plates (identified as Al<sub>n</sub>, were n=1-7) were used. From the data, a clear trend is obtained: higher acidity, prolonged treatment times and higher temperatures favour the coverage and therefore the ceria loading achievable. In Figure 1 the hypothesized reaction pathway and the pictures of the aluminum squares in the plating phases were reported. The reaction takes place few seconds after the dip of the aluminum structures in the bath making gaseous bubbles. After the first hour, gaseous bubbles formation decreases rapidly and within the four hours it ends. These observations can be better understood, if correlated with the reaction pathway proposed by (Arnott et al.1989).

Table 1. XRF evaluation of reaction parameters (pH, reaction time and temperature, number of cycles)

Sample	pH	Time	Cycles	Temperature	Surface weight CeO <sub>2</sub> (%)
Al_1	3	10 min	1	298 K	6
Al_2	3	2 h	1	298 K	10
Al_3	3	4 h	1	298 K	13
Al_4	1	2 h	1	298 K	20
Al_5	1	4 h	1	323 K	24
Al_6	1	4 h	2	323 K	50
Al_7	1	4 h	3	323 K	80

In the first step of the process, at the anodic site of the aluminum surface, there happens the dissolution of the metal surface and evolution of oxygen, whereas at the cathodic site, the reduction of oxygen or hydrogen peroxide induces an increase of the local pH. This increase of pH value gives rise to the formation of cerium hydroxide that react with the aluminum surface to form the characteristic brick red cerium oxide/hydroxide layer. The subsequent drying generates the yellow layer of cerium oxide.

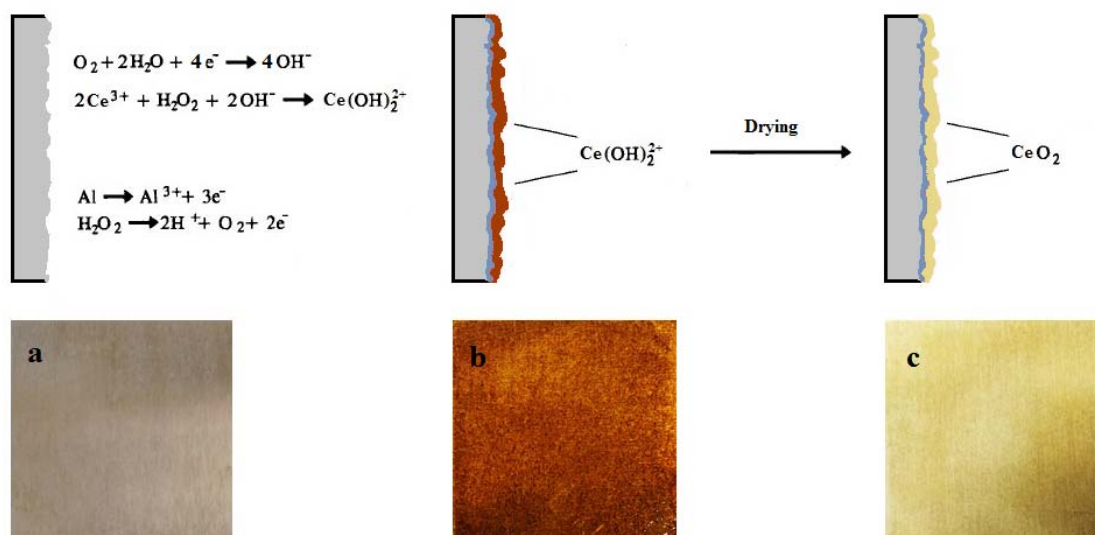


Figure 1. Reaction pathway (top) and pictures of aluminum square as it is (a, after plating (b) and after drying (c)

The deactivation is due to both a rapid decomposition of hydrogen peroxide and a contemporary increasing of the pH value of the bath, for this reason multiple cycles are required to reach higher surface coverage grade. The plated aluminum square were characterized by means of Raman, SEM analysis and ultrasound

adherence test. In Figure 2 the Raman spectrum (a) and the SEM image (b) of Al\_7 were reported. The Raman spectrum essentially showed two peaks, the  $F_{2g}$  mode at  $480\text{ cm}^{-1}$  of ceria fluorite structure type, and a broad peak at  $620\text{ cm}^{-1}$ , attributed to the vibrations induced by the presence of oxygen vacancies. It is interesting to note that the vibration frequency of the  $F_{2g}$  mode, which is normally located in pure ceria at  $464\text{ cm}^{-1}$ , suggesting a change in lattice parameters due to the strong interaction with aluminum surface. The SEM image (Figure 2 b) highlighted the nanometric structure of the ceria coating on the aluminum surface. With the intent to evaluate the mechanical resistance of the coating, the Al\_7 sample was subjected to the ultrasound adherence test. The sample was immersed in petroleum ether and sonicated for 15 minutes, showing weight losses lower than 1 wt %. Looking forward, ceria nanoparticle coating via plating bath procedure represents an attractive solution to realize a ceria nanocoating on metallic surface for catalytic processes (Ho et al., 2018), overcoming the use of a binder between the carrier and the chemical support.

### 3.2. Catalyst characterization and catalytic evaluation

In Table 2 the surface areas, the crystallite sizes and the hydrogen uptake in TPR experiment, for plated foam (CeF40) and catalysed plated foam (PtCeF40), were reported. B.E.T. measurements highlighted the increase of the surface area of the foam support, due to the ceria loading, while the platinum loading did not any effect. The XRD diffractograms of CeF40 and PtCeF40 showed the typical peaks of ceria fluorite-type structure, moreover PtCeF40 diffractogram showed the presence of the peaks of metal platinum. The crystallite sizes were calculated by applying the Scherrer equation to the (111) crystal planes.

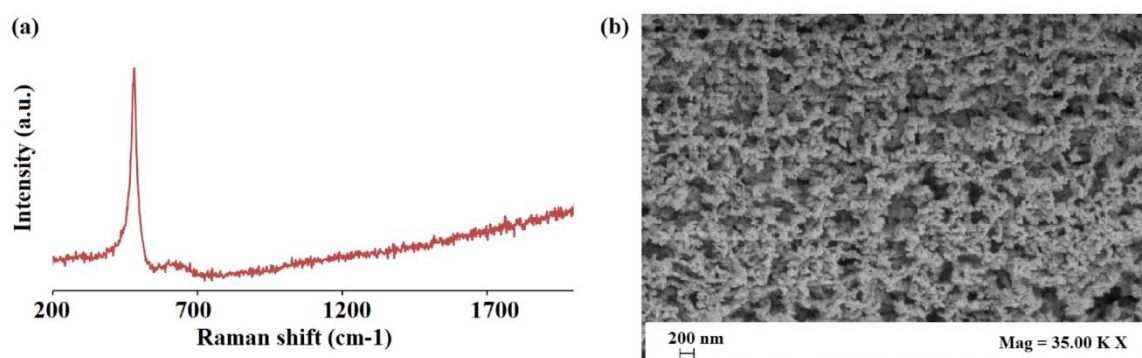


Figure 2. Raman spectra (a) and SEM image of Al\_7 surface (b).

The  $H_2$ -TPR profile (Figure 3 b) showed a large band centred over 600 K, no peaks attributable to  $PtO_x$  species were identified, by confirming the XRD results. In this catalyst platinum persists as a metallic species even in a non-reducing environment, probably because it can be considered as segregated specie or, alternatively because of a contact with the aluminum foam. The consumption of hydrogen, during the TPR experiment, was attributed to the reduction of surface ceria, through the spillover effect (Prins, 2012) from platinum to ceria, demonstrated by a considerably lower reduction temperature compared to that reported for the ceria alone.

Table 2: Surface area, crystallite sizes and hydrogen consumption in  $H_2$ -TPR experiment

Sample	$S_{B.E.T.}$ ( $m^2/g$ )	$H_2$ chemisorbed ( $mmol/g_{cat}$ )	Crystallite Size (nm)	
			$CeO_2$ (111)	Pt (111)
F40	<1	-	-	-
CeF40	8.0	-	8	-
PtCeF40	7.9	0.24	8	22

The catalytic performances were evaluated in terms of CO conversion ( $X_{CO}$ ), calculated as the ratio between reacted and supplied moles, and selectivity to hydrogen, calculated as ratio between hydrogen moles produced and reacted moles of carbon monoxide.

$$X_{CO} = \frac{n_{CO,in} - n_{CO,out}}{n_{CO,in}} \quad (1)$$

$$S_{H_2} = \frac{n_{H_2}}{n_{CO,in} - n_{CO,out}} \quad (2)$$

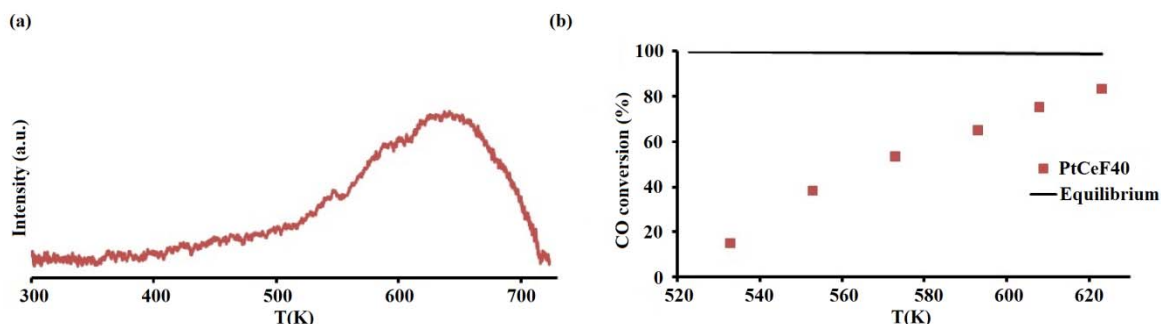


Figure 3.  $H_2$  uptake-TPR profile (a) and CO conversion (b) as function of the temperature for PtCeF40 catalyst.

The PtCeF40 catalyst showed good performance in the evaluated temperature range (520 K – 620 K), the CO conversion exceeded 50 % for temperatures above 560 K, even if it never reached the equilibrium conversion. At lower temperature the catalyst was still active even if by allowing very low CO conversion values, at 530 K the reached value was only 10 %. Anyways, these results are extremely interesting considering the high space velocity used, moreover no methanation reaction was detected at any reaction temperature, highlighting the excellent selectivity to hydrogen that was higher than 98 % into all the investigated temperature range (Palma et al., 2018 c). After the activity test, the weight loss of the catalyst was checked. By results, any loss was not recorded by confirming the excellent coating adherence on the carrier able to hold out at such high temperature too.

#### 4. Conclusions

An alternative method for the preparation of aluminum foam based structured catalysts has been developed and implemented for the water gas shift reaction. The proposed method has been developed on the basis of studies on the plating of the aluminum with cerium oxide, as an alternative to the chromium plating. The preliminary tests, carried out on aluminum squares allowed to set up the plating operating conditions. The results showed that an increase of the reaction temperature, a decrease of pH of the plating bath and more reaction cycles, are able to guarantee a good cerium oxide coating loading. The ultrasound adherence tests highlighted the mechanical resistance of the coating, the SEM images showed the formation of a nanometric ceria coating. This operating procedure was used for the preparation of a structured aluminum foam catalyst. This carrier was firstly coated into the settled up plating bath for a cerium oxide coating and then impregnated into an aqueous solution of tetrammineplatinum (II) nitrate for platinum deposition. The catalyst was characterized by XRD analysis demonstrating the nanometric particle dimensions of ceria and of metallic platinum, the TPR experiments confirmed the advent of an extensive spillover effect ascribable to a good cerium oxide coating with the absence of peaks related to platinum oxide. The activity tests showed that a structured catalyst prepared in such way is able to assure a good CO conversion and hydrogen selectivity at high space velocity.

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