



## Coating of FeCrAlloy foam with Rh catalysts: Optimization of electrosynthesis parameters and catalyst composition

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### ABSTRACT

Coating of FeCrAlloy foam cylinders with Rh-based catalysts was performed by the in situ electrosynthesis of Rh/Mg/Al hydrotalcite-type precursors on the surface of the support. The structured catalysts, obtained after calcination at 900 °C, were characterized and tested in the catalytic partial oxidation of CH<sub>4</sub> at an oven temperature of 750 °C, by feeding diluted and concentrated CH<sub>4</sub>/O<sub>2</sub>/He gas mixtures. Electrochemical parameters (potential applied, synthesis time and supporting electrolyte) and the composition of the catalyst precursor (Rh/Mg/Al atomic ratio) were changed with the aim to optimize both the properties of the coating and catalytic performances. The sample prepared in absence of KNO<sub>3</sub> as the supporting electrolyte at –1.2 V vs saturated calomel electrode for 2000 s yielded the catalyst with the best performances thanks to an improved coating and large amount of Rh in the outer part of the catalytic coating.

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### 1. Introduction

Catalysts coated on three-dimensional ceramic or metallic supports (honeycombs, foams, felts, and fibers) are gaining increasing interest in gas/solid, gas/liquid and gas/liquid/solid processes since the resulting structured catalysts have a high geometric surface area, high mechanical resistance, large void fraction, and minimized pressure drop [1–5]. Moreover, by selecting a support with a high thermal conductivity, the heat transfer of the system is enhanced. Several procedures have been developed to coat both ceramic and metallic supports with catalytically active species [6–8], with the washcoating of ready-made catalysts or supports followed by impregnation of the active phase, being the most widely used procedure [9]. When dealing with metallic supports, the low interaction between metals and ceramic catalysts and the differences in thermal expansion coefficients cause some drawbacks during the preparation procedure. To assure a good adhesion of the film, FeCrAlloy and Inconel supports are usually pretreated by calcination to generate an oxide scale [10,11], acting both as binder between the metal and the ceramic material and as protector of the metal against further oxidation. As an alternative to the washcoating, an electrochemical route has been used with metallic supports, taking advantage of the electrical conductivity of the materials. In particular, the electro-base generation method [12]

has been used to precipitate hydrotalcite-type (HT) compounds on the surface of FeCrAlloy foam cylinders [13–17]. HT compounds are layered materials which – after calcination at high temperature (approx. 900 °C) – generate catalysts constituted by oxide and spinel phases, with a basic character and relatively high surface area, where active species are well dispersed and stabilized [18]. Electrosynthesized Ni/Al and Rh/Mg/Al HT compounds have been used as precursors of catalysts for both the steam reforming (SR) [14] and catalytic partial oxidation (CPO) [15] of CH<sub>4</sub> to produce syngas (H<sub>2</sub> + CO) and/or H<sub>2</sub>.

The partial oxidation of CH<sub>4</sub> is an exothermic process which – in the presence of catalysts, according to a recently proposed mechanism [19,20] – takes place by the exothermic partial and total oxidation of CH<sub>4</sub> at the entrance of the catalyst bed, followed by the endothermic SR of the remaining CH<sub>4</sub>; the water gas shift (WGS) reaction may also occur. The advantages of CPO in comparison to already existing technologies are high CH<sub>4</sub> conversion and selectivity to syngas gas at short contact times, therefore allowing to use small reactors [21–24]. Furthermore, it may be carried out autothermally, and the H<sub>2</sub>/CO ratio obtained is equal to 2, i.e. suitable for the Fischer–Tropsch synthesis. On the other hand, the main drawbacks of this process are harsh reaction conditions, such as high gas hourly space velocity (GHSV) and high temperatures reached in the catalytic bed. In fact, thermal management is considered the main challenge to be fulfilled for the feasibility of CPO in the small scale production of syngas [25].

Ceramic- and metallic-structured catalysts help overcome the main CPO drawbacks. Mostly noble metal-based catalysts (Rh or Pt)

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have been coated on several structured supports such as cordierite [25–29], FeCrAlloy and Nicrofer honeycomb monoliths [30,31], microchannel reactors [32],  $\text{Al}_2\text{O}_3$  [33–38] and FeCrAlloy foams [39], and felts [40]. The performances of the structured catalysts in CPO depend on both the support and the coating catalyst features. The geometry of the support (foam or honeycomb) modified the heat transfer [41]; higher pores per inch for foams [42] and cell density in honeycombs enhanced performances [43]. Moreover, the great heat generated on the upper part of the catalytic bed may be diffused by using a thermally conductive support and consumed by further reforming reactions [43]. With regard to the properties of the coating, the addition of a washcoating support such as  $\text{Al}_2\text{O}_3$  increased Rh dispersion [37,42], while the nature of the deposited catalyst, washcoat loading, and catalyst morphology modified performances [44]. Furthermore, it has been reported how by tailoring the above-commented parameters (pore shape and size, catalyst loading and activity), both the heat management and the presence of hot spots may be controlled [37,45].

In our previous work [15], the electrosynthesis of Rh-containing HT compounds on 8.0 mm diameter FeCrAlloy foam cylinders was performed. Both the cathodic potential applied and the pH of the electrolytic solution appeared to be the main parameters affecting the properties of the electrosynthesized Rh-containing HT compounds. In the present work, our study was extended to coat larger foam cylinders optimizing together with the potential applied and synthesis time the composition of the electrolytic solution (supporting electrolyte and Rh/Mg/Al ratio).

## 2. Experimental

### 2.1. Synthesis of the catalysts

HT compounds were electrosynthesized on a FeCrAlloy foam in a single compartment three electrode cell at room temperature. The working electrode (W.E.) was a 10.0 mm  $\times$  11.9 mm cylinder of FeCrAlloy foam (60 ppi and 4.5% nominal relative density). Foam cylinders were cut from a panel supplied by Porvair (USA). Before the synthesis, foam cylinders were rinsed with ethanol and water. Electrode potentials were measured with respect to an aqueous saturated calomel electrode [SCE; i.e. reference electrode (R.E.)]. The counter electrode (C.E.) was a Pt gauze placed around the foam cylinder at approx. 7.0 mm. The electrical contact was performed by inserting a Pt wire in the middle of the foam cylinder. Electrochemical syntheses were carried out by chronoamperometry with an Autolab PGSTAT128N (Metrohm). The electrolytic solution was an aqueous solution containing the salts of the cations to be precipitated ( $\text{Rh}(\text{NO}_3)_3$ ,  $\text{Mg}(\text{NO}_3)_2$  and/or  $\text{Al}(\text{NO}_3)_3$ ) in the desired ratio (total concentration 0.03 M). The initial pH of the solution was adjusted to 3.8 by adding KOH, according to previous results [15]. When required  $\text{KNO}_3$  (0.3 M) was used as supporting electrolyte. The Rh/Mg/Al atomic ratios (a.r.) in the solution were: 11.0/70.0/19.0 and 13.6/86.4/0.0. Electrosyntheses were carried out at  $-1.1$  V,  $-1.2$  V, and  $-1.3$  V vs SCE for 3000 or 2000 s. After washing and drying at 40 °C, coated foam cylinders were weighed. Catalysts were obtained by calcination of coated foams at 900 °C for 12 h (heating rate 10 °C  $\text{min}^{-1}$ ). The samples prepared in this work are listed in Table 1.

### 2.2. Characterization techniques

The amount of the deposited solid was estimated by weighing foams before and after electrosynthesis. Temperature Programmed Reduction analyses were carried out with a  $\text{H}_2/\text{Ar}$  (5/95 v/v gas mixture, total flow 20 mL/min) in the 60–950 °C temperature range by using ThermoQuest CE Instruments TPDR0 1100. SEM/EDS

analyses were performed by using an EVO 50 Series Instrument (LEO ZEISS) equipped with an INCAEnergy 350 EDS micro-analysis system and an INCASmartMap for imaging the spatial variation of elements in a sample (Oxford Instruments Analytical). The accelerating voltage was 25 kV and the spectra collection time 100 s.

### 2.3. Catalytic tests

Catalytic partial oxidation tests of  $\text{CH}_4$  were carried out in a quartz reactor (i.d. 10.0 mm) operating at atmospheric pressure. Two foam cylinders (10.0 mm  $\times$  11.9 mm) were loaded in the isothermal zone of the reactor. Foams fitted well with the diameter of the reactor to minimize any by-pass. Before tests, catalysts were reduced in situ by an equimolar  $\text{H}_2/\text{N}_2$  mixture (7.0 L/h) for 2 h at 750 °C. Catalytic tests were performed while keeping a constant 750 °C temperature in the oven. The temperature at the inlet of the bed was measured by a chromel–alumel thermocouple placed inside a quartz wire. The effect of both GHSV values and the composition of the gas mixture was studied: GHSV = 11,500, 15,250, 38,700 and 63,300  $\text{h}^{-1}$  (calculated on the total volume of the foam support at STP conditions) and  $\text{CH}_4/\text{O}_2/\text{He} = 2/1/20$  and  $2/1/4$  (v/v). Reaction products were analyzed on-line after water condensation by a Perkin-Elmer Autosystem XL gas chromatograph, equipped with two thermal conductivity detectors (TCD) and two Carbo-sphere columns using He as the carrier gas for the  $\text{CH}_4$ ,  $\text{O}_2$ , CO, and  $\text{CO}_2$  analyses, and  $\text{N}_2$  for the  $\text{H}_2$  analysis. Oxygen conversion was completed in all the experiments.  $\text{CH}_4$  and  $\text{O}_2$  conversions and the selectivity in  $\text{H}_2$  and CO were calculated according to the previously reported formulas [46].

Catalytic tests were repeated twice, with different foam cylinders, in order to check the reproducibility of catalysts. A blank test was performed with bare foam cylinders subjected to a cathodic potential of  $-1.2$  V vs SCE for 2000 s in an aqueous 0.3 M  $\text{KNO}_3$  solution, calcined and reduced under the same conditions as the catalysts. No conversion was observed in diluted reaction conditions, while a small part of  $\text{CH}_4$  converted while feeding the concentrate mixture ( $\text{CH}_4$  conversions of 2 and 5% at 15,250 and 11,500  $\text{h}^{-1}$ , respectively). In this work, every reaction condition was tested for 2 h. The results reported here correspond to mean values when performances were stable, while when catalysts deactivated the results shown correspond to the value of the last test (i.e., the lowest value).

## 3. Results and discussion

### 3.1. Effect of the potential applied ( $-1.1$ , $-1.2$ and $-1.3$ V vs SCE)

The electrosynthesis of hydroxides is based on the generation of a basic medium in the proximity of the working electrode (FeCrAlloy foam) as a result of the reduction of nitrates after applying a cathodic potential to the foam. The pH value depends on the potential applied, with the  $-1.1$  to  $-1.3$  V vs SCE range being suitable for the precipitation of HT phases [14,15]. In our previous work, the best electrosynthesis condition for coating 8.0 mm diameter foam cylinders with Rh/Mg/Al HTs was  $-1.3$  V for 1000 s [15]. In the present work, the diameter of the foam cylinders was increased to 10.0 mm, while a 1000 s synthesis time was not long enough to achieve an acceptable coating. Therefore, in order to improve the degree of coverage of the foam, syntheses were performed at  $-1.3$  V for 2000 s, but the catalyst showed poor performances (not shown). Longer synthesis time promoted both the generation of  $\text{H}_2$  bubbles, which detached the coated solid, and led to the deposition of a large amount of potassium, which covered the active sites. Therefore, in this paper, we introduced changes in synthesis parameters to avoid both drawbacks.

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