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Coprecipitated-like hydrotalcite-derived coatings on open-cell metallic foams by electrodeposition: Rh nanoparticles on oxide layers stable under harsh reaction conditions

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ABSTRACT

Structured catalysts based on open-cell metallic foams coated by a catalytic film offer a great potential for intensification and optimization of catalytic processes. Here, we demonstrated the feasibility of the electrodeposition to synthesize in situ and quick Rh/Mg/Al hydrotalcite-type (HT) syngas catalyst precursors with controlled composition, morphology and thickness around 5 to 20 μm on the surface of FeCrAlloy foams using a two-compartment flow electrochemical cell. After calcination at 900 °C, catalytic coatings with properties similar to those of conventional co-precipitated HT-derived catalysts were identified by synchrotron nano-XRF/XRD tomography and HRTEM. The resulting structured catalysts, therefore, merged the properties of both HT-derived catalysts and open-cell foams, namely, thermally stable nano MgO- and spinel-type phases where Rh was dispersed and stabilized against sintering, and high mass and heat transfer. Moreover, the development of a $MgAl_2O_4$ thin film in the support-coating interface, by chemical reaction between Mg^{2+} from the coating and Al^{3+} from the support during calcination, increased the catalyst adhesion. Consequently, active and stable performance was obtained under harsh reaction conditions in the catalytic partial oxidation of CH_4 to syngas as a model reaction. Even in the catalysts operating under severe reaction conditions for about 50 h, the coating was stable and Rh metallic nanoparticles around 2 nm were still well dispersed.

1. Introduction

Structured catalysts made of a 3D support coated by catalytic species have gained increasing attention since their initial application in automotive exhaust gas treatment [1,2]. The development of supports of different shapes (open-cell foams, fibers), materials (ceramic and metallic, including high corrosion resistant alloys) as well as experimental and modelling studies demonstrated the ability of these type of materials to enhance mass and heat transfer and decrease pressure drop, making them the best option for catalytic processes operating at high gas hourly space velocities, and/or strongly endo-/exothermic [1,2]. In particular, open-cell metallic foams provide a disruptive and tortuous flow path and hence a high flow mixing as well as supply or release of the heat to/from the surface in comparison to honeycomb monoliths, showing advantages in H_2 and syngas production by reforming and partial oxidation [3,4], CH_3OH and Fischer-Tropsch synthesis [3,5,6], and CO_2 methanation [4,7]. For instance, in the exothermic and fast catalytic partial oxidation (CPO) of CH_4, the pressure drop and formation of hot spots can be decreased with structured catalysts in comparison with their pelletized counterparts, thus enhancing the activity and stability of the catalysts [8–11].

The first step in the development of structured catalysts is the deposition of a highly active catalytic film, with suitable thickness, homogeneity and adhesion to the support. The stability of the coating determines the catalytic activity and in metal-based structured catalysts also the resistance to oxidation of the metal supports [12–14]. Hydrotalcite-type (HT) compounds, layered materials with general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2](A^{n-})_{x/n}$ mH_2O are widely used as catalyst precursors, and in particular for syngas production processes [15]. Hence, they were applied as catalytic coatings on honeycombs, open-cell foams, and fibers for the steam reforming [16], oxy-reforming [17], dry reforming [18], partial oxidation [19,20], and ethanol reforming [21].

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The well-known dip-coating of catalyst slurries or the in situ precipitation of HT compounds have been proposed to prepare structured catalysts. The former method can deposit large catalyst loadings on metallic monoliths (ca. 20 wt%) through long procedures adding additives to the coating, which can modify the catalyst and decrease catalytic performance [22]. The washcoating of foams is more challenging: to avoid pore clogging, low density slurries are used, decreasing the catalyst loading on SiC foams to 1–4 wt% [23]. On the other hand, vertically aligned HT platelets can directly grow on the structured support, i.e. a Ni foam, through homogeneous urea precipitation under hydrothermal conditions [17]. For anodized Al supports, i.e. Al_2O_3/Al, the substrate is the Al source and, besides urea [24,25], NH_3 [26,27] can be used as a precipitating agent. In these cases, the adhesion of the HT compounds vertically grown on the surface of the supports is improved. However, compared to coprecipitated catalysts, the structured ones show worse reducibility and lower catalytic activity in the total oxidation of ethanol, due to the formation of spinel-like phases, high structural ordering of the products deposited on the Al_2O_3/Al supports, and differences in composition [25]. Moreover, in these methods the precipitation of HTs can take place not only on the surface of the structured support but also in the bulk of the solution, which is a drawback especially for noble metal-containing catalysts.

The electrodeposition, specifically the electro-base generation method, is “ideally” the best way to coat metallic supports in situ with HT-type materials [28,29]. Unlike the above commented precipitation methods, the pH increases quickly and near the surface of the support due to the reduction of nitrate, oxygen and water by application of a cathodic potentiostatic pulse [30]; therefore, the solid is selectively precipitated on the support in a short time. Thus, we proposed this technique to synthesize HT compounds in situ on FeCrAlloy open-cell foams to prepare structured catalysts for the catalytic partial oxidation (CPO) of CH_4 to syngas [19]. However, the control of the composition is challenging, as nominal and real compositions deviate. For instance, during the preparation of thick Rh/Mg/Al HT coatings (10–15 μm), we observe the sequential precipitation of layers with different compositions as the synthesis time proceeds, which modifies composition, crystalline phases, Rh reducibility and metal particle size and, consequently, film stability and catalytic performance [31,32].

The challenging preparation of these Rh/Mg/Al HT films can be related to the formation of thick and insulating layers, and the inefficient replenishment of the electrolytic solution on the surface of the electrode at long times [30]. Although differences in the precipitation pH, diffusion coefficients of the cations and the shape of the support could also play a role in this phenomenon. Indeed, deviations in the expected composition of Ni/Co- [33–35] and Fe-containing compounds [36–38] deposited on Ni foams are reported notwithstanding thin films are prepared at short times. To the best of the authors’ knowledge, only one article reports the coating by Fe-Co hydroxides of Ni foams with controlled composition by continuous electrodeposition at a constant current density of 10 mA cm^{-2} for 1800 s [39].

In porous supports, such as open-cell foams, limited mass transfer inside the pores, and generation of polarization potentials or changes in the local current density do not guarantee a uniform composition and thickness of deposits over the complete geometry [40,41]. Electrodepositions performed under forced convection, by pumping or agitation, and through pulse depositions, with stirring between the pulses, can improve the properties of the coating. The mechanical stirring replenishes the electrolytic solution and decreases the thickness of the diffusion layer during the electrodeposition [42,43]; however, in the coating of complex shaped supports an inhomogeneous flow rate and hence strongly scattering current density can be generated, creating inhomogeneity in the coating [44]. The use of short electrochemical pulses, allowing sufficient time (aided by stirring) between depositions, replenishes the local ion concentration creating a more homogeneous Fe distribution in Ni-Fe/Oxihydroxide on a Ni foam as well as modifying the texture of the film [45]. Finally, the use of flow cells improves the mass transfer in the preparation of ZnO over Cr and Au electrodes [46] and Cu on 3D graphite felts [47] by replenishing the solution inside the felt.

The aim of this work was to control the electrodeposition of Rh-containing HT compounds on the surface of small pore open-cell metallic foams. The final goal was to obtain, after calcination, a stable coating with controlled properties (i.e. Rh loading, thickness, Rh metallic particle size and dispersion) not possible until now, to further improve the activity and stability of structured catalysts for syngas production. To achieve that, the electrodepositions were performed under flow in a homemade flow-cell double-compartment electrochemical set-up. To study the feasibility of the procedure, two Rh/Mg/Al samples with different Rh loading (2 and 5% as atomic ratio) were prepared, like in our previous work [32], the high Rh loadings were used to balance the low amount of catalytic coating. The catalysts were tested in the CPO of CH_4, and characterized at the different stages of their life-time by XRD, electron (FE-SEM, HRTEM) and synchrotron combined nano-XRF/XRD tomography, which allowed to study the distribution of the elements and crystalline phases in the coating and the foam support in the nano-scale rather than in the micro-scale previously reported by us [12,13].

2. Experimental section

2.1. Catalyst preparation

All chemicals were purchased from Sigma Aldrich: $Mg(NO_3)_2{\cdot}6H_2O$ (> 99%), $Al(NO_3)_3{\cdot}9H_2O$ (> 98%), $Rh(NO_3)_3$ solution (10 wt% Rh in HNO_3). FeCrAlloy open-cell foam cylinders (80 ppi, pores per inch, and 10 mm × 11.9 mm), cut from a panel, were used as structured supports.

Electrodepositions were performed in a homemade double-compartment flow electrochemical cell by FAVS Gnudi, using a potentiostat (Autolab, PGSTAT128N, Eco Chemie) with GPES software. A Pt coil (0.4 mm diameter and 40 cm in length) and a saturated calomel electrode (SCE) were used as counter and reference electrode (C.E. and R.E.), respectively. The working electrode was the FeCrAlloy foam in the cylindrical shape and it was assembled by a three-pronged Pt electrical contact as described elsewhere [31]. The working and counter electrode compartments were separated by a glass frit tube to avoid the mixture of the electrochemical reaction products. The reference electrode was in electrolytic contact with the main compartment via a Luggin capillary placed close 1 mm to the surface of the foam cylinder. All potentials were reported with respect to SCE. Prior to coating, the foam was subsequently washed in acetone, water and then dried at 60 °C for 24 h.

The electrodepositions were performed by circulating the electrolyte during the coating process in the working electrode chamber with a flow rate of 2 mL min^{-1} by a peristaltic pump. Preliminary studies indicated that a lower (or no) or higher flow gave poorer results in terms of coating properties and catalytic activity. The synthesis conditions (potential applied, time and composition of the electrolytic solution) were like those used in depositions performed in the conventional single-compartment cell, i.e. a -1.2 V vs SCE pulse was applied for 2000 s to the foam immersed in an aqueous metal nitrate solution (0.06 M) containing Rh/Mg/Al atomic ratio (a.r.) 5/70/25 or 2/70/28 [32], named Rh5 or Rh2 respectively. It should be noted that in these electrolytes, the set-up reached a low uncompensated resistance (R_u) ca. 1–2 Ω in all of experiments. After electrodeposition, the coated foams were thoroughly washed with distilled water and dried at 40 °C for 24 h. The samples were then calcined at 900 °C for 12 h with a 10 °C min^{-1} heating rate.

2.2. Characterization techniques

Scanning electron microscopy (SEM) coupled to energy dispersive spectrometry (EDS) was performed by using an EP EVO 50 Series