



Novel Rh-based structured catalysts for the catalytic partial oxidation of methane

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ABSTRACT

Novel Rh-based structured catalysts were prepared by the electrosynthesis of Rh/Mg/Al hydrotalcite-type (HT) precursors on a FeCrAlY foam. The catalysts obtained by the calcination of HT compounds were investigated in the catalytic partial oxidation (CPO) of CH₄. The effects of the electrosynthesis conditions (potential and pH of the plating solution) on the surface morphology and chemical composition of the samples as well as on the catalytic activity were investigated. The control of the pH of the solution favoured the precipitation of Rh as hydroxide rather than of metallic particles, whereas the potential applied determined the pH value reached near to the foam. By increasing the cathodic potential from −1.2 to −1.3 V, but keeping the synthesis time constant (1000 s), the required conditions to obtain HT precursors were achieved faster and, therefore, a larger amount of them precipitated. Due to the different coverage and chemical nature of the electrosynthesized species, catalytic performances depended on the synthesis conditions, the best values being achieved by the catalyst obtained from the HT precursor prepared at −1.3 V for 1000 s.

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1. Introduction

The catalytic partial oxidation (CPO) of methane to syngas (CO + H₂) is a slightly exothermic reaction in which high methane conversion and syngas selectivity are achieved at short contact times, making it possible to use small reactors [1–3]. For these reasons, CPO may be used to obtain syngas in small-medium scale plants, i.e. to produce it for distribution. Pelletized catalysts consisting of Ni, Co and noble metals on several supports such as Al₂O₃, MgAl₂O₄, CeO₂–ZrO₂ are widely used [4]. However, due to both the high gas-hourly-space-velocity (GHSV) values adopted and the high temperatures reached in the catalytic bed, the mechanical stability of the catalyst and its thermal conductivity play a key role in the development of the process. In this sense, structured catalysts [5] can be useful thanks to their large geometric areas, low pressure drop and high mechanical stability. In addition, by selecting structured supports with high void fractions, thermal conductivity, and convective heat transfer, both the formation of hot spots and the “run away” of the reaction may be avoided [6], as the large amount of heat generated on the upper part of the catalytic bed can be diffused by the metallic support and consumed by further reforming reactions [7].

Bulk metal structured catalysts, such as noble metal gauzes or sponges [8–10] and nickel foams [11,12] have been applied in CPO, although they show low surface area values. On the other hand, structured catalysts in which the active catalyst is deposited on a ceramic or metallic support – such as alumina foams [13–19], extruded cordierite or α -alumina honeycomb monoliths [9,20–26], felts [27], FeCrAlloy and Microfer metallic monoliths [28–30] as well as a FeCrAlloy metallic foam [31] – lead to a significant reduction of the amount of catalyst, without a decline in the catalytic performances. In structured catalysts, the amount and dispersion of the active phase can be controlled by changing either the thickness of the coating or the metal loading. Furthermore, the performance of the catalyst is determined by the synthesis procedure, morphology and stability of the film. Different synthetic procedures have been used to coat the supports and obtain CPO catalysts: (i) impregnation or coprecipitation of the salts of the active metals (Rh, Pt or Ni) on alumina-structured supports [15,18,19,22] or impregnation of the elements to form Zr_{0.8}Ce_{0.2}O₂ and LaNi_{0.9}Pt_{0.1}O_x phases [26]; (ii) wash-coating of a primer and subsequent impregnation or coprecipitation of the active phase [9,17,20,25]; (iii) wash-coating of a ready made catalyst [27]; (iv) microwave-assisted combustion synthesis of Pt nanoparticles on Al₂O₃ foams [32]. The coating of metallic supports with a ceramic catalyst is not straightforward, since the adhesion of the layer to the support is low and problems can arise during drying and calcination; therefore, the major challenge is in achieving a homogeneous and well-adhered catalyst layer on the monolith walls [33]. In some cases it has been reported that the addition of a primer or the treatment of the sup-

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port at a high temperature in an oxidizing atmosphere improve the adherence of the catalyst to the support [34,35].

The electrodeposition can be used to deposit hydroxides and/or oxides on metallic supports through the base-electrogeneration method, which consists of the generation of a basic pH near the support by the reduction of an easily reducible anion, like NO_3^- or ClO_4^- [36,37]. This technique, largely used for the preparation of modified electrodes, has been extended to the preparation of catalysts [38–40]. Recently, some of the authors proposed the electrosynthesis and deposition of hydrotalcite (HT)-type compounds, precursors of Ni-based catalysts active in the steam methane reforming [41–43]. HT compounds are layered materials [44,45] that, after calcination, lead to mixed oxides with the active phase well distributed and after reduction small and stable metallic particles are obtained. In particular, HT compounds containing Ni, Co and noble metals have been used as precursors for the CPO of methane [46,47]. In the present study, the base-electrogeneration method has been extended to the preparation of Rh/Mg/Al HT compounds on a FeCrAlY alloy foam, which are precursors of Rh-based catalysts for the CPO of methane [48]. The effects of the pH of the plating solution and potential applied on both the coating properties and the catalytic activity are investigated. Moreover, the aim of this work was to compare the activity of the electrosynthesized catalysts with that of a Rh-based pelletized catalyst with the same structure, it means, obtained from HT compounds.

2. Experimental

2.1. Synthesis of the catalysts

Rh/Mg/Al- NO_3 HT compounds were electrosynthesized on a FeCrAlY foam by cathodic reduction of a solution containing metal salts and KNO_3 . The Rh/Mg/Al atomic ratio in the solution was 11/70/19, with a total concentration of 0.03 M. The synthesis was performed at two different pH values of the plating solution: (i) 2.1 that corresponds to the pH obtained by adding nitrates to water and (ii) by adjusting the pH with NaOH to 3.8. Electrochemical deposition was carried out at room temperature (r.t.) using a single compartment, three-electrode cell. Electrode potentials were measured with respect to an aqueous saturated calomel electrode [SCE; i.e. reference electrode (R.E.)]. A Pt gauze was used as counter electrode (C.E.). The working electrode (W.E.) was the FeCrAlY foam (80 ppi and 5% nominal relative density). FeCrAlY foam pellets were obtained by cutting cylinders of 8 mm diameter and 10 mm long from a panel. Electrochemical tests were recorded using a CH instrument Mod. 660C controlled by a personal computer via CH Instrument software. Electrosynthesis was carried out at two different potentials -1.2 and -1.3 V vs SCE for 1000 s. The precursors were named as follows: RhHT-X, where X = potential applied (-1.2 , -1.3). When the pH of the plating solution was controlled at 3.8 the label “pH” was added at the end of the name (e.g. RhHT-1.2pH). Electrosynthesis in the same conditions was also carried out on FeCrAlloy plates to allow a complete characterization of the deposited material. After electrodeposition, the films were gently rinsed with double-distilled water and then dried. The catalysts were obtained by calcination at 900°C for 12 h of coated foam pellets. The catalysts were named by replacing HT by exHT in the label (e.g. RhexHT-1.2pH). For comparison purposes, a low loaded Rh-based powder catalyst was also prepared by calcination of a HT precursor Rh/Mg/Al (0.1/80/19.9 atomic ratio) containing silicates in the interlayer region; further details on the synthesis are reported elsewhere [49]. The amount of Rh was ca. 0.2 wt.%.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were collected with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) by means of a X'PertPro PANalytical diffrac-

tometer equipped with a fast X'Celerator detector. The $3\text{--}80^\circ 2\theta$ range was measured performing steps of $0.07^\circ (2\theta)$ and counting 120 s/step. The analyses were performed on a powder that was gently removed from a FeCrAlloy plate. A “zero background” sample holder (The Gem Dugout, State College, PA, USA) was used. Temperature Programmed Reduction and Oxidation (TPR/O) analyses were carried out with a H_2/Ar or an O_2/He (5/95 v/v) gas mixture, respectively (total flow rate 1.2 L/h) in the $100\text{--}950^\circ\text{C}$ temperature range by using ThermoQuest CE Instruments TPDRO 1100. Covered metallic foam pellets were used directly for measurements. 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, the beam current 1.5 nA, and the spectra collection time 100 s. Specific surface area measurements were carried out in a Micromeritics ASAP 2020 instrument by N_2 adsorption/desorption at -196°C . The values are given with respect to the total weight of the structured catalyst (foam + catalyst). Samples were previously degassed under vacuum, heated up to 200°C and maintained at this temperature for 30 min.

2.3. Catalytic tests

Catalytic tests were carried out in a quartz reactor (i.d. 8 mm) operating at atmospheric pressure. Two cylinders of the foams ($8 \text{ mm} \times 10 \text{ mm}$) were loaded in the isothermal zone of the reactor. The foams fit well with the diameter of the reactor to minimize any by-pass. Catalysts were reduced in situ before the tests in an equimolar H_2/N_2 mixture (7.0 L/h) for 2 h at 500°C for the RhexHT-1.2 catalyst and at 750°C for the RhexHT-1.2pH and RhexHT-1.3pH catalysts. Catalytic tests were performed keeping the temperature of the oven (T_{oven}) constant at 750 and 500°C and allowing the temperature of the catalyst to vary depending on the endothermicity/exothermicity of the process. The effect of the GHSV values and the concentration of the gas mixture was studied: GHSV = 28,000 and $120,000 \text{ h}^{-1}$ (calculated on the total volume of the foam support) and $\text{CH}_4/\text{O}_2/\text{He} = 2/1/20$ and $2/1/4$ (v/v). No large pressure drop was observed during the tests. The catalytic activity of the coated foam pellets was compared with that of a Rh-based pelletized catalyst (average size $600 \mu\text{m}$). The tests were performed loading the same weight of the pelletized catalyst than that of the coated foam and feeding the same flow of reactants, keeping therefore the flow/weight (F/W) ($\text{cm}^3/\text{g h}$) constant. The gas phase temperature was measured by a moveable chromel–alumel thermocouple sliding in a quartz wire inside the catalytic bed. The maximum temperature (T_{max}) and that at the outlet of the catalytic bed (T_{out}) were measured. The reaction products were analysed on-line after water condensation by a PerkinElmer Autosystem XL gas chromatograph, equipped with two thermal conductivity detectors (TCD) and two Carbosphere columns using He as the carrier gas for the analysis of CH_4 , O_2 , CO and CO_2 and N_2 for the H_2 analysis.

3. Results and discussion

3.1. Characterization

As previously reported for Ni/Al electrosynthesized HT precursors on metallic foams [43], no blockage of the pores occurs. SEM images of the sample prepared at -1.2 V in 1000 s without adjusting the pH of the plating solution, pH = 2.1, indicate that the sample is rather inhomogeneous, as also observed by a visual inspection of the foams. During the electrosynthesis, the whole or a part of the foam turns black, instead of the yellow colour characteristic of Rh^{3+} , pointing out its reduction to Rh^0 . A SEM image of some

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