



Original carbon-based honeycomb monoliths as support of Cu or Mn catalysts for low-temperature SCR of NO: Effects of preparation variables

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ABSTRACT

A series of catalysts consisting in Cu or Mn supported on lab-scale carbon-based honeycomb monoliths, which have been previously prepared following an original methodology, have been investigated in the low-temperature selective catalytic reduction of NO with NH₃. Special attention has been paid to the effect of changing different preparative variables for the incorporation of the active phase: way of introducing the metal, concentration of the precursor solution and time of contact with the monoliths in the case of impregnation, use or not of a chemical pre-treatment of the support, and the final drying procedure. Complementary techniques employed for the chemical, textural and structural characterisation have revealed significant differences between the catalysts depending on their preparative procedure.

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1. Introduction

Carbon, especially upon activation, is traditionally one of the most commonly employed materials for adsorption applications due to its porosity properties [1]. Nevertheless, it is seldom used as catalytic support of honeycomb monoliths type [2], as compared to powder, granules, spheres, extrudates, pellets and tablets. Thus, although a monolithic reactor would offer clear advantages in relation to a conventional packed bed such as less pressure drop and easier handling [3,4], carbon rheological properties render difficult its extrusion [5].

In previous works however we demonstrated that, with the use of appropriate additives, obtaining carbon-based monoliths is not only possible but also easily controllable following methodologies originally developed for ceramic materials [6–8] that allow optimizing the composition of the carbonaceous dough in order to be extruded. Further we showed that the resulting monoliths were potential candidates as VOCs adsorbents after being activated [8]. The present work aims to investigate the application of the obtained carbon monoliths as support of metal active phases for environmental catalysis applications. In particular, different samples constituted by copper or manganese supported on

carbon-based lab-scale honeycomb monoliths have been prepared for the selective catalytic reduction (SCR) of NO with ammonia. This reaction is one of the favourite applications of monoliths for gas phase catalysis [9,10]. Besides this, the combination of carbon as material support and metal oxides (V, Fe or Mn, and even Cu although much less investigated) as active phase has been recently proposed for the NO-SCR as interesting alternatives respect the commercial V₂O₅-WO₃/TiO₂ [11]. The reason is that carbon-based catalysts show high activity around 200 °C instead of the usual operation conditions (300–400 °C) allowing to be placed in the downstream where there is a less aggressive atmosphere concerning particles concentration and SO₂ content. The use of carbon in the formulation for NO-SCR catalysts have been previously investigated but in the form of carbon-coated cordierite monoliths [12].

The main scope at this stage was to study the influence of the metal phase incorporation procedure on its final state besides the texture and structure of the catalysts as all these properties are crucial for the application of any heterogeneous catalyst [13]. In particular, it is well known that in order to obtain a good distribution besides an acceptable dispersion of the active phase great care must be taken in the catalysts preparation [14], particularly in the monolithic design in which the amount of active phase related to the total volume of catalyst is much lower compared to powder beds or extrudates [9]. For this reason the following preparative variables were investigated: (1) the way of introducing the metal [15]; (2) the

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concentration of the precursor solution in those catalysts prepared via impregnation technique; (3) the time of contact between the monoliths and such solution; (4) the use or not of an acid or acid/basic chemical pre-treatment of the support [16]; (5) the final drying method, conventional or microwaves assisted [17].

To the best of our knowledge no similar work is found in literature, dealing with the study of the effect of the preparation method on metal supported on carbon-based monoliths, especially with a wide variety of complementary characterisation techniques as here employed, that give information concerning composition, texture, chemical behaviour and particularly fine details of the materials structure, being only available references related with washcoated cordierites as support [17,18].

2. Experimental

2.1. Materials

The carbon-based honeycomb monoliths used in the present work were prepared from a medium volatile bituminous coal provided by the National Institute of Carbon in Spain, whose composition was 30 wt% of volatile and less than 6 wt% of ashes, and 75 vol% of vitrinite phase concerning its maceral composition. Its extrusion was achieved according to a previously reported methodology [6,7] using the following additives: 9.5% silicate clay (ARGI-2000 from VICAR, S.A.), 2.5% glycerine, 1.9% methylcellulose, and 0.3% aluminium phosphate dissolved in *o*-phosphoric acid (weight percentages referred to the extrudable paste excluding water). The plastic properties of the extrudable dough were liquid limit = 47% and plasticity index = 24%, parameters defined and measured according to previous references [19]. After extrusion the green monoliths were dried at 80 °C overnight and submitted to preoxidation (air, 250 °C, 24 h), carbonization (Ar, 840 °C, 1 h) and finally, activation (H₂O, 250 Torr/Ar, 860 °C up to a burn-off degree of 15%). The resulting honeycomb monoliths had the following geometric characteristics: square section, 13.7 cells/cm², 0.08 cm of wall thickness, a geometric surface area of 10.4 cm²/cm³ with 49 % open frontal area.

Regarding the metal precursors two nitrate salts were employed: Cu(NO₃)₂·3H₂O from PANREAC, S.A. and Mn(NO₃)₂·4H₂O from Sigma–Aldrich with 99% and 98.5% of purity, respectively.

2.2. Catalyst preparation

Three different preparation methods have been used for metal introduction on carbon-based honeycomb monoliths: (1) impregnation with the precursor solution, (2) integration in the paste before the extrusion step, and (3) homogeneous deposition-precipitation from urea decomposition. In the first case the concentration of the precursor solution was adjusted to 1 or 2 M, and different times of contact with the monolith were tested: 30, 60, and 90 min. In some cases a pre-treatment of the support with a 65 wt% HNO₃ solution during 1 h at 60 °C followed or not by an additional treatment with a 0.05-M NaOH solution for 1 h at room temperature was applied before the metal impregnation. The resulting impregnated samples were dried either conventionally (in an oven at 90 °C overnight) or using microwaves (500 W, 1 min). For the sake of clarity the following nomenclature has been adopted to identify each sample according to its preparation method: first the metal symbol, then the initials “int” or “dp”, if the catalyst is prepared by integration or deposition-precipitation, respectively, or three numbers in the case of impregnation which denote consecutively the lack of support pre-treatment (0) or its existence (acid, 1 or acid/basic, 2), the precursor solution concentration and the contact time; finally, a letter (conventional, C or microwaves assisted, M) which indicates the

drying method, followed by an asterisk in those samples in which there is no final metal activation. As an example, Cu 0.1.30.M would refer to a copper catalyst prepared by impregnation of a non pre-treated monolith with a 1-M nitrate precursor solution during 30 min which has been finally dried using microwaves and subjected to final activation of the metal according to the procedure further indicated.

The Cu int catalyst was prepared adding 15 ml of a 4-M precursor solution in three steps to 50 mg of the extrudable carbonaceous paste. After extrusion and drying overnight at 100 °C under synthetic air flow, the resulting monolith was calcined in Ar at 400 °C for 1 h. The Cu dp catalyst was prepared by immersing the carbon-based monolith support in a mixture of 10 ml of a 0.1-M precursor solution and 15 ml of a 1-M urea solution and heating at 90 °C during 10 h. Afterwards the monolith was dried in an oven at 90 °C overnight.

2.3. Characterisation techniques

Textural characterisation has been carried out by physical adsorption of N₂ at –196 °C in a Micromeritics ASAP 2020 using its software utilities for the data reduction. Scanning Electron Microscope (SEM) images and EDS data have been obtained using a Quanta 200 scanning electron microscope (Philips) equipped with a Phoenix Microanalysis system using a nominal resolution of 3 nm. Induced coupled plasma spectroscopy (ICP) analysis of the chemical composition was performed using an IRIS Intrepid HR instrument. X-ray diffraction (XRD) was carried out at room temperature using a Bruker D8-500 powder diffractometer operating with Cu K α radiation and the Rietveld analysis of the data was performed using the Fullprof program [20]. Thermogravimetric analysis was carried out both under air or He flow with a TA thermobalance, model SDT Q600, using 25 mg of crushed samples and a heating rate of 10 °C/min. Complementary temperature programmed desorption (TPD), reduction (TPR) and oxidation (TPO) experiments were performed employing a Thermostat QMS 200 (Pfeiffer) mass spectrometer with a 60 ml/min flow of He, H₂-5% or O₂-5%, respectively, and using also milled pieces of monoliths (50 mg) and 10 °C/min as heating rate.

2.4. Catalytic activity tests

The evaluation of the catalysts activity was performed in a stainless steel continuous flow reactor of 1.35-cm internal diameter and an internal sample holder with allows preventing the gases from bypassing the monolith. A 0.90 ± 0.05-cm edge square section and 4-cm long monolith was used for each test and a pre-treatment consisting on heating at 250 °C in a 120-ml/min He flow for 1 h was applied before running the experiments, according to the below described study, with exception of Cu int for which the temperature chosen was 400 °C. The experiments consisted in heating the sample under the reactant mixture up to 500 °C using a rate of 5 °C/min. Reaction conditions were selected considering previous similar experiences of other authors with lab-scale monoliths [21–23]. The gas composition was 3000 ppm NO, 6000 ppm NH₃, 2 vol% O₂ balanced by He and N₂. The total flow rate was 345 ml/min, which corresponds to a GHSV of 6390 h⁻¹. NO concentration in the outlet gases were continuously measured in a NGA 2000 Fisher Rosemount CLD analyzer module using a chemiluminescence detector.

3. Results and discussion

3.1. Thermal analysis

Prior to any other study, thermal analysis of the metal-containing monoliths was performed in order to know their

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