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Carbon-based catalysts: Synthesis and applications



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ABSTRACT

This paper summarizes the main results obtained by the Fuel Combustion Group in three applications: (1) carbon-based catalysts for the selective catalytic reduction (SCR) process of NO_x, (2) Pt and Pt–Ru catalysts for direct alcohol fuel cells, (3) carbon-supported catalysts for the electroreduction of CO₂. Concerning the first aspect, low-cost catalysts able to work at lower temperatures have been prepared and compared with commercial catalysts; for the second one, new catalysts for methanol and ethanol electrochemical oxidation exhibiting current densities that are double those of the commercial ones have been developed; as regards the third one, carbon-supported catalysts for the electroreduction of CO₂ based on Fe and Pd were synthesized and tested. Formic acid was obtained as the main product on all Fe/C electrodes.

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1. Introduction

Carbon materials have been used as catalysts for many years. Activated carbons have been considered over the last decades for their utilization in several processes involving heterogeneous catalysis, because they have suitable support properties, as inertness toward unwanted reactions, stability under regeneration and reaction conditions, adequate mechanical properties, modifiable surface area, porosity, and physical form, i.e., the possibility of being manufactured in granulates and conglomerates of different sizes and shapes to suit different chemical reactor configurations [1–4].

However, ACs present two important limitations: their narrow microporosity, which makes difficult mass transport processes and the lack of electrical conductivity,

which prevents their use as electrocatalysts. In order to overcome these limitations, new synthetic nanostructured carbon materials such as nanotubes, nanofibers, nanocoils, nanohorns and ordered mesoporous carbons have been developed during the last decade, as new catalyst supports that present several advantages versus activated carbon: they have a better pore structure, more uniform characteristics, a reduced number of impurities and a better electronic structure [4]. Thus, a wide field of applications has been deployed for these materials because they possess electrical and thermal conductivity, as well as a mechanical strength and lightness that conventional materials cannot match [2,5].

The Fuel Conversion Research Group of ICB–CSIC has a long track record in the preparation and characterization of carbon materials [6–15]. In a first stage, ACs obtained from low-rank coals were tested as catalysts and catalyst supports in energy-related reactions such as sulfur and nitrogen emissions reduction from coal combustion and gasification. It was shown that the textural properties and,

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in particular, the surface chemistry of these materials, which is controlled by the presence of oxygen groups, were well suited to carry out such reactions.

With the arrival on the scene of renewable energies, in particular renewable electricity, the interest in the conversion energy processes moved toward the electrochemical reactions involved in electrochemical devices such as fuel cells and solar fuels harvesting by means of CO₂ electrochemical reduction. Activated carbons are not adequate for these applications due to their lack of electrical conductivity and their narrow microporosity, so new carbon materials intended to overcome these limitations were synthesized: carbon nanofibers (CNF), nanocoils (CNC), and xerogels (CXG), as well as ordered mesoporous carbon materials (OMC) and carbon blacks (CB), e.g., the commercial material Vulcan XC-72R, have been synthesized and used as catalytic supports for different applications [6–39]. Carbon materials have been obtained using different methods. In the case of carbon nanofibers, they were synthesized by methane decomposition on a NiCuAl₂O₃ catalyst. This catalyst was prepared by co-precipitation of the metal nitrates, followed by a calcination process at 450 °C. Later, a methane flow is passed through a furnace containing the catalyst at 700 °C for 10 h, transforming this molecule into molecular hydrogen and carbon deposited in nanofiber shape. On the other hand, carbon nanocoils were synthesized by the catalytic graphitization of a resorcinol–formaldehyde gel. In this procedure, formaldehyde and silica sol were dissolved in deionized water. Then, nickel and cobalt salts mixtures were added before the addition of resorcinol as an organic precursor. This mixture was heat-treated at 85 °C for 3 h and dried at 108 °C. Finally, it was carbonized in a nitrogen atmosphere at 900 °C for 3 h. Removal of silica particles was achieved by a chemical treatment with a concentrated NaOH solution, followed by a treatment with concentrated HNO₃. For the synthesis of carbon xerogels, resorcinol, water, formaldehyde and sodium carbonate were mixed under stirring in ratios that promote the obtaining of highly porous xerogels. The mixture was put into closed vials and cured for 24 h at room temperature. After that, the vials were heated in an oven at 50 °C for 24 h and dried at 85 °C for 120 h. The pyrolysis of the organic gels was performed at 800 °C during 3 h under an N₂ flow. Finally, ordered mesoporous carbons were obtained by incipient wetness impregnation method using ordered mesoporous silica as a template and a furan resin/acetone resin as a carbon precursor. Silica was impregnated with the carbon precursor and after carbonized at 700 °C for 2 h. Subsequently, the silica–carbon composite was washed with NaOH in ethanol to remove the silica. Further details can be found elsewhere [6–15]. From these works, carbons with different physicochemical properties have been obtained. Thus, CNF and CNC show a crystalline structure with well-aligned graphene layers, while OMCs exhibit a hexagonal ordered structure composed of amorphous carbon. In contrast, CXG are mainly composed of non-crystalline carbon aggregates, which are characterized by the random aggregation of primary carbon spheres. All these materials present different textural properties, with a surface area increasing in the order

CNF < CB < CNC < CXG < OMC, covering a wide interval of values from 70 m²·g⁻¹ for carbon nanofilaments, due to their lack of microporosity, to 1050 m²·g⁻¹ for OMC. This last material presents a very developed surface area, which is associated with their porous structure based on periodic carbon cylinders, with uniform mesopores between them.

Although the activated carbons and the mesoporous carbons described above present very different textural properties, their surface chemistry present many similarities because each of them is controlled by the presence of oxygen groups. As a consequence, their acid–base and redox properties and therefore their performances as a catalyst can be studied with analogous physicochemical criteria.

In this summary of the keynote presented at the AWPAC 2014 (3rd International Symposium on Air & Water Pollution Abatement Catalysis), the results obtained in three different applications related to the topics of the conference are presented:

- carbon-based catalysts for the selective catalytic reduction of NO;
- Pt and Pt–Ru catalysts for direct alcohol fuel cells;
- carbon-supported catalysts for CO₂ electroreduction.

2. Carbon-based catalysts for the selective catalytic reduction of NO

Nitrogen oxides, NO_x, have a huge impact on our environment. They generate acid rain, soil eutrophication and acidification, as well as water nitrification, and also they contribute to ozone formation in the lower layers of the atmosphere. They are generated in every combustion process making use of a fossil or N-containing fuel and/or, most importantly, when combustion takes place under air atmosphere at high temperatures (> 900 °C). Increasingly stricter environmental regulations concerning the emission of nitrogen oxides (NO_x) have forced the development of more efficient technologies to reduce the emission of these pollutants from small and medium industrial facilities. Activated carbons have been used as catalysts in De-NO_x after-treatment technologies. They can act as a NO_x reductant itself [40,41], as a catalyst or as a catalyst support, either in the presence or in the absence of an external reducing agent.

The selective catalytic reduction (SCR) is the reduction of nitrogen oxide in the presence of a catalyst and a reducing agent. The use of carbon-based catalysts in this process has been studied in the last years, because they are able to bring down the optimal reaction temperature for achieving high De-NO_x conversions in comparison to TiO₂-based catalytic systems. Several carbon materials have been impregnated with Cu [42,43], Fe [42], Mn [44–46] and V compounds [20,21,47].

Catalysts containing vanadium as active metal supported on activated carbons were extensively studied by Lázaro et al., investigating as well the use of petroleum coke ashes as a V-source [21]. The authors optimized [22] the features of the activated carbon support, modifying several parameters in the preparation process via steam activation of a low-rank coal. They observed that adequate

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