

Reseña Tesis. CO₂ Valorization by electrochemical reduction using catalysts supported on nanostructured carbon materials

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OBJECTIVES AND NOVELTY

CO₂ reutilization by the electrochemical route is a well-known possibility for the valorization of CO₂-rich gas streams, leading to the production of valuable chemicals and fuels. The electrochemical reduction of CO₂ has been widely studied on bulk metals suspended in different electrolytes. However, several technological aspects must be still solved, such as the high overpotentials required to reach a reasonable CO₂ reduction rate, the low CO₂ solubility and the strong H₂ formation as a by-side product by water reduction. In addition, the development of electrodes with high activity and product selectivity remains a key challenge and the reaction mechanism is not clear. These limitations could be solved combining: (i) The use of advanced catalytic systems based on metal nanoparticles supported on nanostructured carbon materials (NCMs), which represents a powerful strategy to increase the active surface area and to tune the activity/selectivity of the process. These supported catalysts may be further deposited on a carbon substrate obtaining 3D porous electrodes (gas diffusion electrodes, GDEs), which allow a better CO₂ distribution on the active phase. (ii) The development of fundamental studies on the mechanism to advance in the design of effective catalysts. In situ spectro-electrochemical techniques should be used to study on line the electrochemical performance and to detect the reduction products/intermediates. (iii) The use of an electrocatalytic reactor operating in gas phase, instead of the conventional systems based on liquid phase reactions. This challenging approach avoids the problem of the low CO₂ solubility and minimizes the H₂ evolution.

This PhD Thesis deals with these three key aspects with the main aim of **gaining a fundamental understanding of CO₂ electroreduction using electrodes based on nanostructured carbon materials**. In order to achieve this main aim, the following specific objectives were addressed:

1. Synthesis and characterization of NCMs:

Different NCMs were synthesized for being tested in the electrochemical reduction of CO₂: carbon nanofibers (CNFs), carbon nanocoils (CNCs), and ordered mesoporous carbons (OMCs). The commercial carbon black Vulcan XC-72R (conventionally used as electrocatalyst support) was also used. In addition, a study of the influence of the progressive introduction of oxygen-containing species on Vulcan XC-72R was carried out, which enhance the anchoring of metal nanoparticles. The NCMs were spectro-electrochemically characterized by differential electrochemical mass spectrometry

(DEMS); i.e. a mass spectrometer *in situ* coupled to an electrochemical system. This technique allows following *in situ* the electrochemical properties of the electrodes and, simultaneously detecting the products/intermediates from CO₂ reduction.

2. Development of electrocatalysts supported on NCMs for CO₂ electrochemical reduction:

Catalysts based on noble (Pt and Pd) and non-noble (Fe, Cu, Co and Ni) metals were developed for CO₂ reduction. The synthesized NCMs were used as support. The electrochemical performance of the electrodes was analyzed in detail in acid (0.5 M H₂SO₄) and neutral media (0.1 M NaHCO₃).

3. Fabrication and spectro-electrochemical characterization of GDEs:

GDEs were obtained depositing the synthesized electrocatalysts on a carbon cloth. The resulting electrodes were spectro-electrochemically characterized by a novel DEMS configuration.

4. Electrochemical reduction of CO₂ in gas phase:

An electrochemical reactor was designed and developed for CO₂ reduction in gas phase. Selected electrodes were tested in the reactor.

RESULTS

Carbon supports for the electrochemical reduction of CO₂

NCMs with different morphology and structure were synthesized and characterized for being used in the CO₂ electroreduction: graphitic CNFs and CNCs and OMCs which consist of a hexagonal ordered structure composed of amorphous carbon (Figure 1). DEMS studies showed a lower cathodic current and an inhibition of the hydrogen evolution in presence of CO₂, which is explained by the adsorption of species derived from CO₂ reduction (CO_{2,red}) at carbon surfaces. However, the formation of adsorbates occurred at more negative potentials for the commercial carbon.

In addition, a study of the influence of O functionalization of Vulcan XC-72R on the electrochemical behaviour was performed. The carbon black was subjected to different oxidation treatments with nitric acid (Nc) or a nitric-sulphuric mixture (NS) at room (Ta) or boiling (Tb) temperatures during 0.5 or 2 hours. Oxygen-containing species were progressively introduced on the carbon surface as the severity of the oxidation conditions was increased (NSTa0.5 < NcTb0.5 < NcTb2). By comparison of the voltammograms in the absence and presence of CO₂, an inhibition of the hydrogen

evolution was showed. A strong current decrease, and consequently, a higher adsorbate amount, was observed on Vulcan and the samples treated with Nc (65-78%), while that the adsorption of CO_2 occurred to a much lesser extent on the carbon treated with NS due to its higher contribution of basic groups (obtained by TPD) which seem to inhibit the formation of adsorbates.

Carbon-supported electrocatalysts for the electrochemical reduction of CO_2

A wide variety of electrocatalysts, involving different metals (Pt, Pd, Fe, Cu, Ni and Co), synthesis routes and oxidation states, were prepared and the response toward the CO_2 reduction established. A strong adsorption of species derived from CO_2 reduction was obtained in all the carbon-based catalysts, which seems to be promoted by the use of a carbon support. These species are likely to be CO_{ad} and other adsorbates (COOH_{ad}). In particular, catalysts based on Pd supported on NCMs (CNFs, CNCs, OMCs and Vulcan XC-72R) were prepared to study the influence of the carbon nature. All Pd/C catalysts effectively reduced CO_2 to other adsorbed species. However, a different catalytic activity was observed depending on the support due to differences in the Pd- H_{ad} strength.

Catalysts based on non-noble metals supported on Vulcan and amorphous oxides of magnetite/maghemite and crystalline CuO and Cu_2O were also studied. An inhibition of the hydrogen evolution was showed for all (metal and oxide) catalysts. A strong current decrease, and consequently, a higher

adsorbate amount, was observed on copper-oxides (75-85 %) vs. the metal catalyst (45 %).

Gas diffusion electrodes for the electrochemical reduction of CO_2

GDEs were prepared from the carbon-supported electrocatalysts and their performance for CO_2 conversion was analysed by DEMS by a novel set-up. In this context, it is the first time that GDEs are spectro-electrochemically characterized by DEMS for CO_2 reduction. Electrodes based on iron-oxide catalysts (magnetite/maghemite) were studied. Vulcan, before and after oxidation treatments, was used as support. DEMS studies showed that formic acid/formaldehyde was obtained on all the Fe/C electrodes at room conditions. Formic acid may be used as fuel and it presents several applications for agriculture, chemical, and pharmaceutical industries. Furthermore, it was shown that the activity toward CO_2 reduction depended significantly on the carbon surface chemistry. Indeed, oxygenated groups enhanced the catalytic activity for CO_2 reduction to formic acid (Fe/Vulcan_NcTb0.5 and Fe/Vulcan_NSTa0.5) in comparison to the electrode supported on the bare material (Fe/Vulcan). However, the GDE treated in nitric acid during 2 hours (Fe/Vulcan NcTb2) presented the lowest formic acid generation despite the high O amount, which is explained by the partial collapse of the porous structure (evidenced by N_2 physisorption).

A novel electrochemical reactor for CO_2 conversion in gas phase

An electrochemical reactor was designed to perform

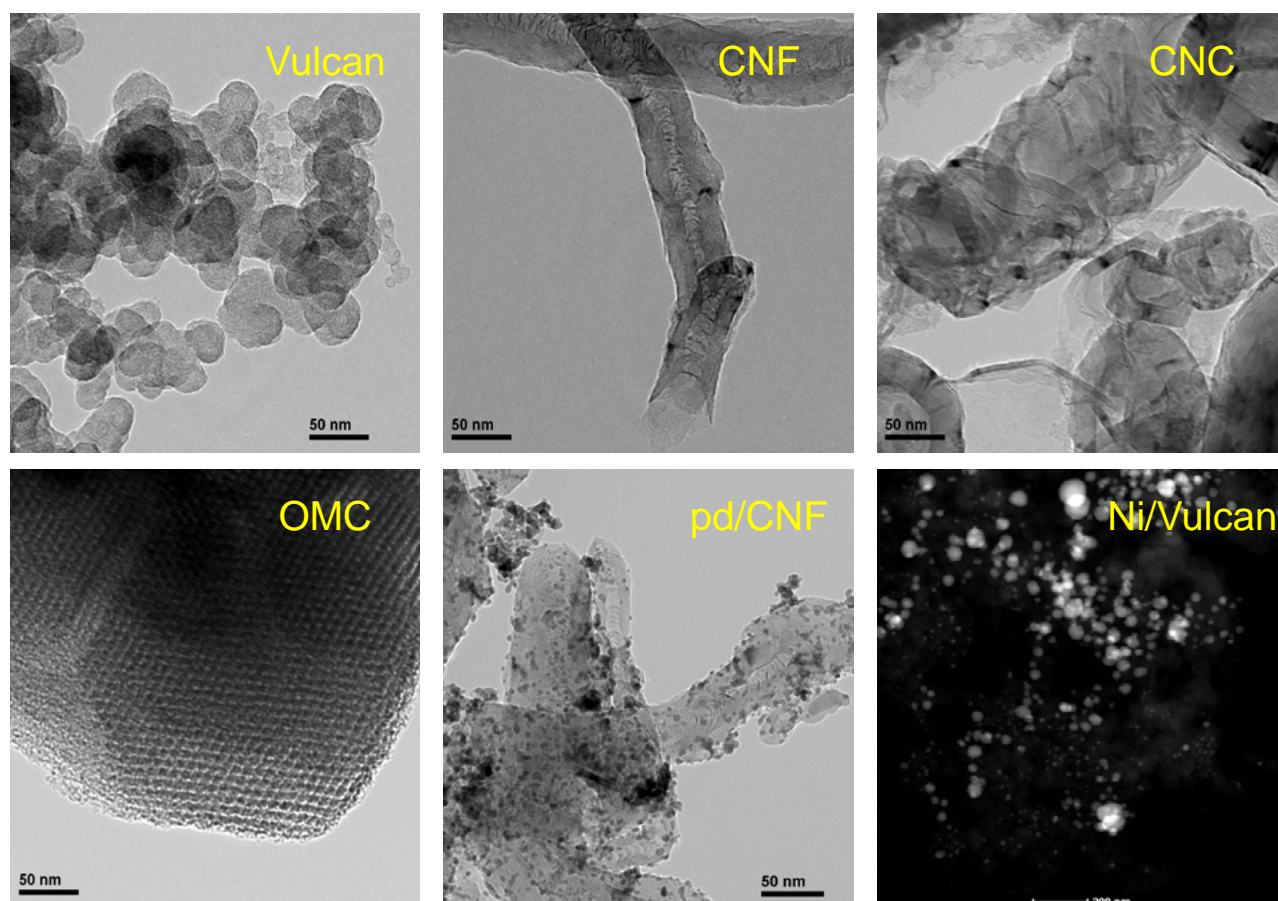


Figure 1. TEM/STEM micrographs of the carbon supports and selected catalysts.

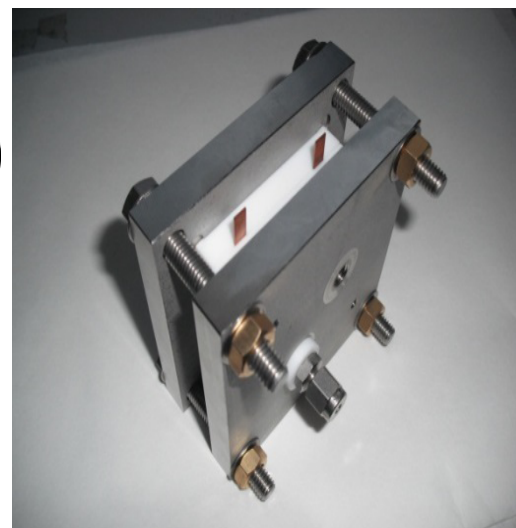
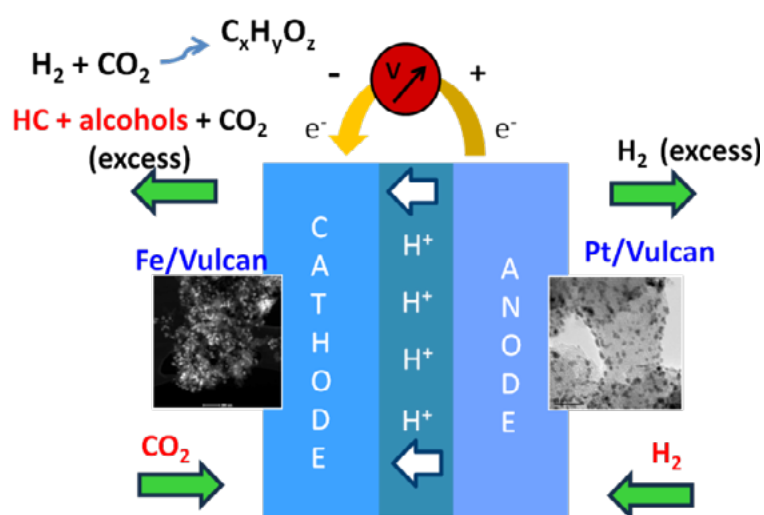


Figure 2. Scheme and photograph of the designed electrochemical reactor for CO₂ electroreduction in gas phase

CO₂ in gas phase (Figure 2).

The reactor, which presents a technology similar to a polymer electrolyte membrane fuel cell, consists of two GDEs, anode and cathode, separated by a polymer membrane. On the anode H₂ is oxidized to protons and electrons, which are used in the cathode side to reduce CO₂. An electrode based on a Fe oxide catalysts supported on Vulcan was used as cathode due to its exceptional efficiency for CO₂ conversion to formic acid in acid media. An electrode based on a commercial Pt/Vulcan catalyst was also employed for comparison. This electrode was always used in the anode. A higher current density was developed for the Pt-based electrode due to a significant formation of H₂ by the water reduction, whereas the CO₂ conversion was favored on the Fe electrode.

CONCLUSIONS

The obtained electrodes supported on nanostructured carbon materials were effectively used in the electrochemical reduction of CO₂. In addition, it was demonstrated that the nature of the carbon support and its oxygen functionalization present a strong impact on the activity and selectivity toward the electrochemical reduction of CO₂. Thus, obtained results confirm the potential of the application of electrodes based on carbon-supported catalysts for the CO₂ reduction back to useful products.

RELATED PUBLICATIONS

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