



Carbon - iron electro-catalysts for CO₂ reduction. The role of the iron particle size



Jesica Castelo-Quibén^a, Abdalla Abdelwahab^{a,1}, María Pérez-Cadenas^b, Sergio Morales-Torres^a, Francisco J. Maldonado-Hódar^a, Francisco Carrasco-Marín^a, Agustín F. Pérez-Cadenas^{a,*}

^a Carbon Materials Research Group, Department of Inorganic Chemistry, Faculty of Sciences, University of Granada Campus Fuentenueva s/n, ES18071 Granada, Spain

^b Department of Inorganic and Technical Chemistry, Science Faculty, UNED, Paseo Senda del Rey 9, ES28040 Madrid, Spain

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ABSTRACT

Different types of carbon-iron electro-catalysts have been prepared, exhaustively characterized, and tested as cathodes for the electro-catalytic reduction of CO₂ at atmospheric pressure. Commercial iron and graphite sheets have also been tested as cathodes for comparison.

All these electro-catalysts promoted the formation of C1 to C4 hydrocarbons showing a high selectivity to C3 hydrocarbons within this group of compounds. The iron particle size seems to be a very important parameter involved in the hydrocarbon formation. A linear correlation between mean iron particle sizes determined by XRD and the faradaic efficiency of the materials has been found: the smaller the iron particle size, the higher the faradaic efficiency. Iron nano-particles smaller than 4 nm increased significantly the formation of hydrocarbons.

1. Introduction

The high CO₂ atmospheric concentration is one of the major environmental concerns because it is the main cause of global warming [1]. There are different strategies trying to control this issue [2], being the CO₂ storage and the CO₂ transformation to other valuable products the most extended, together with the implement of the renewable energies.

Renewable energy sources such as solar, wind and tidal electricity are receiving also a lot attention but they do not produce the constant and tunable currents that fossil fuels provide. Storage of surplus electrical energy produced during peak production periods and its release during peak demand periods is thus crucial, especially as both peak production and peak demand periods often do not coincide. In this way, the electro-catalytic reduction of CO₂ can be an alternative strategy to address both problems, storing temporary and local surpluses of renewable energy [3,4] while CO₂ is transformed in valuable hydrocarbons.

The direct electrochemical reduction of CO₂ in aqueous solution has been typically studied with metal electrodes like Cu, Au, or Sn during the past few decades [5–10]. More recently, metallic electrodes derived from corresponding metal oxides, like SnO_x, seemed to promise certain catalytic performance for CO₂ reduction [11–13], and only a few transition-metal oxides such as TiO₂, FeO_x and Cu₂O have been

reported as potential electro-catalysts for this application [14].

Meanwhile, different type of materials and nano-materials are being tested as cathodes [15], carbon-based materials are among the most widely investigated [13,16–20]; in particular iron-carbon catalysts [18,20,21] are claiming attention as electro-catalysts for CO₂ reduction to hydrocarbons.

Several studies have been concerned with elucidating the mechanism of electro-reduction of CO₂ to hydrocarbons, which could be related with a Fischer-Tropsch mechanism of chain propagation [22,23].

Within the carbon materials, carbon xerogels and aerogels are nanostructured materials obtained from the carbonization of organic gels, which are prepared by the sol-gel polycondensation of certain organic monomers, typically resorcinol (R) and formaldehyde (F) [24]. The textural characteristics of these materials strongly depend on a careful control of the reactant concentrations and the experimental conditions of the different synthesis steps: gelation, curing, drying and carbonization/activation [25–27]. The addition of surfactants during the R-F polymerization strongly affects the morphology of these materials and the final metal dispersion [28]. Therefore, surface area, pore volume, and pore size distribution are tuneable properties related to the synthesis and processing conditions, enabling the preparation of a wide suite of materials with unique properties, e.g. for adsorption [29,30], catalytic [31–34] and electrochemical applications [35–37]. Moreover,

* Corresponding author.

E-mail address: afperez@ugr.es (A.F. Pérez-Cadenas).

¹ Present address: Material Science and Nanotechnology department, Faculty of Postgraduate Studies for Advanced Science, Beni Suf University, Beni-Suef 62511, Egypt.

carbon gels doped with transition metals show a high dispersion and homogeneous distribution of the metals throughout the carbon matrix [38–41]. The majority of metal cations will be anchored into the structure of the carbon gel, which minimizes the leaching of the metals in liquid phase applications. Nevertheless, a percentage of the metal phase of the doped carbon gels will not be accessible to the reactants, although preparation techniques are available that minimize this issue [42].

Fe-, Cu- and Ni-doped carbon xerogels have been tested as working electrodes in the electro-catalytic reduction of CO₂ to hydrocarbons. Although all doped xerogels formed mainly methane (CH₄), the selectivity varied depending on the type of doping metal used [37]. Recently [35], carbon aerogels and xerogels doped with different cobalt loadings also have been tested as cathodes for this reaction. The cobalt-carbon phases formed in these types of doped carbon gels improved the selectivity to C3-C4 hydrocarbons formation, obtaining even more yield of C3 hydrocarbons than CH₄ in some cases.

In the present work, several types of carbon gels and an innovative carbon xerogel – carbon nanofiber composite were doped with iron and then, applied as electro-catalysts in the reduction of CO₂ to hydrocarbons. The effects of different iron contents, porosity and iron mean particle size of these electro-catalysts, on their activity and selectivity in the reduction of CO₂ to hydrocarbons, are studied and discussed.

2. Experimental

Iron-doped carbon gels were prepared by dissolving resorcinol (R) and formaldehyde (F) in water (W) and using the corresponding metal acetate as catalyst precursor (C). The used (R/F) and molar ratio (R/W) were 1:2 and 1:17 respectively. Different amounts of C were used in order to obtain two different Fe loadings (1 and 6 wt.%, approx.) among de final carbon aerogels and xerogels. The mixture was stirred to obtain homogeneous solutions that were cast into glass moulds and cured 1 day at 40 °C, and 5 days at 80 °C, obtaining the corresponding wet organic gels. Then, the organic gels were introduced in acetone to exchange the solvent media [26]. Two different drying processes, supercritical CO₂ or thermal oven, were carried out in order to obtain the dry organic sample: aerogel (A) or xerogel (X), respectively. Finally, all the organic gels were carbonized in a N₂ flow at 900 °C during 5 h, and using a heating rate of 1 °C/min. The prepared carbon gels will be referred as follow: AFe1, XFe1 and XFe6, being 1 and 6 the weight percentage of metal loading in the aerogel and xerogel samples. On the other hand, a second type carbon xerogel, hereafter as XFe6b, was obtained avoiding the exchange with acetone before the thermal drying. An additional material was prepared by heating sample XFe6b at 700 °C in H₂ flow during 1 h, and after that, the H₂ flow was changed in situ by a mixture of He:C₂H₄:H₂ with a volumetric ratio of 90:10:20, respectively, keeping the same temperature during 2 h. In these conditions, carbon nanofibers (CNFs) grew on the carbon xerogel matrix forming therefore a carbon xerogel-CNF composite, labelled as XFe6bNF. A 50–50 wt.% carbon xerogels – CNF composition was estimated by weighting the materials after the different steps, including only after the H₂ pre-treatment; in this last case, obviously a specific portion of sample was used only for this weight calculation.

The iron contents of the electro-catalysts were determined by burning off a portion of the sample at 800 °C in air and weighting the residue.

The characterization of the samples was carried out using physical adsorption of nitrogen, mercury porosimetry, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Raman, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and linear sweep voltammetry (LSV).

The porous texture was analyzed by N₂ adsorption at –196 °C. Prior to measuring the N₂ adsorption isotherms, the samples were outgassed overnight at 110 °C under high vacuum (10^{–6} mbar). The BET equation was applied to the N₂ adsorption data from which the apparent surface

area, S_{BET}, was obtained. The Dubinin-Radushkevich (DR) equation was applied to the N₂ adsorption data in order to obtain the corresponding micropore volume (W₀) and micropore mean width (L₀). Total pore volumes (V_{0.95}) are calculated from N₂ adsorption isotherms at –196 °C and at 0.95 relative pressure. Finally, the BJH method [43] was applied to the desorption branch of the N₂ adsorption isotherms to obtain the mesopore volumes (V_{BJH}) and mean mesopore widths (L_{BJH}).

Mercury porosimetry was obtained up to a pressure of 2320 kg/cm² using Quantachrome Instruments equipment model POREMASTER 33. Macropore volumes, V_{MACRO}; and the pore size distributions from 6.5 nm, PSD, were obtained with this technique. Prior to the analysis the samples were outgassed.

SEM was performed using a Zeiss SUPRA40VP scanning electron microscope, equipped with secondary electron detector, back-scatter electron detector, and using a X-Max 50mm energy dispersive X-ray microanalysis system. All the samples were crushed before realizing this analysis.

HRTEM was carried out using a FEI Titan G2 60–300 microscope with a high brightness electron gun (X-FEG) operated at 300 kV and equipped with a Cs image corrector (CEOS) and for analytical electron microscopy (AEM) a SUPER-X silicon-drift window-less EDX detector.

Raman spectra were obtained using a Micro-Raman JASCO NRS-5100 dispersive spectrometer with a 532 nm laser line.

XRD patterns were recorded with BRUKER D8 ADVANCE diffractometer using CuKα radiation. JCPDS files were searched to assign the different diffraction lines observed. Diffraction patterns were recorded between 5° and 70° (2θ) with a step of 0.02° and a time per step of 96 s. The average crystal size (d_{XRD}) was determined using the Scherrer equation.

XPS measurements of the fresh samples were performed using a Physical Electronics ESCA 5701 equipped with a MgKα X-ray source (hν = 1253.6 eV) operating at 12 kV and 10 mA, and a hemispherical electron analyser. For these measurements, the binding energy (BE) values were referred to the C_{1s} peak at 284.7 eV. A base pressure of 10^{–9} mbar was maintained during data acquisition. Survey and multi-region spectra were recorded at C_{1s}, O_{1s} and Fe_{2p} photoelectron peaks. Each spectral region of interest was scanned several times to obtain good signal-to-noise ratios. The spectra obtained after background signal correction were fitted to Lorentzian and Gaussian curves in order to obtain the number of components, the position of each peak and the peak areas.

Electro-catalytic conversion of CO₂ was carried out in a three-electrode cell of 300 cm³ of capacity at ambient temperature and pressure. A Biologic VMP multichannel potentiostat was used to induce electro-catalytic reduction by applying adequate potential differences over the electrodes. A platinum electrode was employed as a counter electrode, and Ag/AgCl as reference electrode. A CO₂-saturated 0.1 M potassium bicarbonate aqueous solution (150 cm³) was used as electrolyte. The setup was used in potentiostatic mode at –1.65 V, reproducing the voltage conditions of previous works, using Ag/AgCl as reference electrode [23]. Prior to the electro-catalytic CO₂ reduction, the solution was saturated with CO₂ by bubbling through for 3 h. After saturation, the pH of the solution was 6.7. The CO₂ feed and exit lines were closed off, and the reactor was operated in batch mode. The amount of carbon gel used as electro-catalyst in the working electrode (cathode) was 80 mg which was homogeneously pasted on both sides of a graphite sheet with dimensions of 50 mm × 8 mm. In the preparation of the working electrode the carbon gel was mixed with the corresponding amount of polytetrafluoroethylene (PTFE) in a weight ratio of (80:7) using a PTFE (60%) water solution. Working electrodes were kept in 0.1 M potassium bicarbonate aqueous solution overnight before being used in the electro-reactor. All electro-catalysts were also tested carrying out the reaction under Ar-saturated solution, and therefore using electrolytes free of CO₂.

All electro-catalysts were characterized by LSV. The cathodic sweep analysis was conducted from the equilibrium electrode potential to

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