Noble metal-free catalysts supported on carbon for CO₂ electrochemical reduction

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Abstract

In the present work, a wide variety of electrocatalysts, involving different metals, synthesis routes and oxidation states, have been prepared and the response towards the CO₂ reduction on carbon-supported established. In particular, catalysts based on non-noble metals (Cu, Co, Fe and Ni) supported on carbon black (Vulcan XC-72R) were tested in the electrochemical reduction of CO₂. Amorphous oxides of magnetite/maghemite and crystalline CuO and Cu₂O oxides obtained by different methodologies were also studied. Previously, the efficiency of the catalysts for the hydrogen formation was evaluated in 0.1M NaHCO₃ since it takes place as a competitive reaction during CO₂ reduction in aqueous electrolytes. By comparison of the voltammograms in the absence and presence of CO₂, an inhibition of the hydrogen evolution was showed for all (metal and oxide-based) catalysts due to the adsorption of species from CO₂ reduction (CO_{2,red}). Interestingly, the CO_{2,red} formation on Co and Fe-surfaces operating under these conditions has not been stated before. A strong current decrease, and consequently, a higher adsorbate amount, was observed on copper-oxides (75-85 %) vs. the metal catalyst (45 %).

Keywords: carbon-supported catalysts, noble metal-free catalysts, CO₂ electrochemical reduction, H₂ evolution reaction.

1. Introduction

The electrochemical reduction of CO₂ has been studied for many years using different metal electrodes since the product distribution strongly depends on the used material [1-3]. Efficient catalysts for CO₂ reduction should provide both the activation of CO₂ and the subsequent hydrogenation to reduced species. For this reason, metals with low hydrogen overpotentials, such as Pt and Pd, have been widely used since these materials adsorb easily hydrogen [4-7]. Adsorbed hydrogen favours the adsorption of species derived from CO₂ on the electrode surface, since the formation of "reduced CO₂" adsorbates requires interaction between CO₂ molecules and adsorbed hydrogen [4, 5, 7].

Cu has attracted also special attention since hydrocarbons, aldehydes and alcohols were obtained on this metal at significant current densities [3, 8-10]. Other non-noble metals (such as Fe, Co, Ni) have been also studied due to their low cost [1, 11, 12]. However, these electrodes show low electrocatalytic activity for CO₂ reduction in aqueous solutions and room conditions, obtaining H₂ (by water reduction) as major product in the potential reduction region [1, 11, 12]. However, at low temperatures (ca. 2°C), high pressures (ca. 30 atm) and/or using non-aqueous solvents, the electrocatalytic rate toward the CO₂ reduction increases and the product distribution may change [9, 13-16]. In this context, Azuma et al. [16] reported that the CO₂ reduction efficiency increased dramatically on some metal electrodes (such as Ni) as the temperature decreased. On the other hand, the formation of formic acid and CO together with short and long chain hydrocarbons (methane, ethane or propane) has been reported on Fe, Co, and Ni electrodes [13-15]. Similarly, Ohta et al. [17] reported the formation of methane, carbon monoxide and ethane, on different metal electrodes (among them Fe, Co and Ni) using methanol into the supporting electrolyte.

Other strategy could be the use of their corresponding oxides to enhance the efficiency for CO₂ conversion or the selectivity [18-23]. For example, Huang et al. [18] reported a high yield to formate from the photoelectrochemical reduction of CO₂ on an electrode based on Co₃O₄. Similarly, methanol has been detected as the major product at high current densities on Cu₂O-based electrodes [20-22] and even the formation of hydrocarbons has been reported in Cu₂O films [23]. Finally, Kanan and co-workers [19] observed a decrease of the overpotential for CO₂ reduction and a higher stability on a Cu/Cu₂O in comparison to bare Cu.

Most of these studies have been carried out involving bulk electrodes and the use of carbon-supported catalysts has not been widely extended [24-31]. These electrodes may increase the local CO₂ concentration due to their nanoporous structure, enhancing the reduction rate. Consequently, the activity and selectivity could be modified in comparison to that obtained with bulk catalysts.

Regarding the preparation of carbon-supported catalysts, different synthesis routes have been reported in bibliography, including impregnation, colloidal and microemulsion methods [32-34]. Among them, the impregnation route is the most extensively used due to its simplicity and good results. Several reducing agents have been used involving liquids, such as borohydride [35], ethylene glycol [36], formic acid [37] and hydrazine [38] or gases, hydrogen [39]. The experimental conditions (e.g. temperature, reducing agent, solution pH, etc.) present a strong influence on the properties of the resultant catalysts, such as the size, dispersion, structure or the chemical state of the active phase. Consequently, the performance of the electrocatalysts may be modified varying the synthesis route [32, 39].

In this work, different non-noble metal (Ni, Cu, Co and Fe) catalysts supported on the commercial carbon black Vulcan XC-72R (which is usually used as catalyst

support for electrochemical applications) have been tested for the electrochemical reduction of CO₂ in 0.1 M NaHCO₃. A Pt/Vulcan catalyst was also studied for comparison. In addition, catalysts based on copper and iron oxides have been also obtained using different synthesis routes with the purpose of analyzing the effect of the oxidation state on the performance for CO₂ reduction. The electrochemical activity of the catalysts efficiency of the catalysts for the hydrogen formation was also evaluated since it occurs as a competitive reaction during CO₂ reduction in aqueous electrolytes.

2. Experimental

2.1 Synthesis of carbon-supported catalysts

Carbon-supported electrocatalysts were prepared by three different impregnation methods: reduction of metal precursors with (i) borohydride (BH) and (ii) ethylene glycol (EG), and incipient-wetness impregnation and reduction with hydrogen (WI).

Different metals or their corresponding oxides were selected as active phase, including noble (Pt) and non-noble (Fe, Cu, Co and Ni) metals. The commercial material Vulcan XC-72R (supplied by Cabot) was used as the electrocatalysts support.

Appropriate amounts of metal precursors (Table S1) were employed to obtain a theoretical metal loading of 20 wt.% onto the corresponding carbon material. The synthesized catalysts were denoted as A/Vulcan_B where A and B refer to metal and synthesis method, respectively. For example, the nomenclature used for an electrocatalyst based on Cu supported on Vulcan and reduced with borohydride is Cu/Vulcan_BH. A summary of the carbon-supported electrocatalysts prepared by the different impregnation routes is shown in the supplementary information (Table S2).

It is important to note that noble metal-free catalysts were prepared by the WI method when a metallic active phase was required, while BH or EG routes were used

for the deposition of Cu or Fe oxides.

2.1.1 Incipient-wetness impregnation and reduction with hydrogen (WI method)

An aqueous solution of the metal precursor is employed to permeate the pores of the carbonaceous support. Then the metal is reduced using H_2 as reducing agent. The WI route consists of the following steps: first, the metal precursor (0.4 M) is dissolved in a H_2O – $EtOH$ 1:1 (v/v) mixture under mechanical stirring. The solution volume was 4 mL in order to greatly exceed the total pore volume of the support ($S_{BET} = 0.38 \text{ cm}^3 \text{ g}^{-1}$ obtained by N_2 -physisorption [30]). A known amount of the support (400 mg of Vulcan XC-72R to obtain 500 mg of the corresponding catalyst) was gently impregnated with the metal solution. Afterwards, the resultant samples are dried overnight at 70 °C and then reduced at 650 °C in presence of H_2 (total flow = 65 mL min⁻¹, 15% H_2 and 85% N_2) for 2 hours. At the end of the reduction time, the reactor is slowly cooled under N_2 flow to room temperature.

2.1.2 Reduction with borohydride (BH method)

In this route, electrocatalysts are prepared by impregnating the carbonaceous support with the metal precursor solution. Subsequently, the metal is reduced with sodium borohydride. The procedure consists of the following steps: first, an aqueous solution of the metal precursor (10 mM) is slowly added to a dispersion of the carbon support in ultrapure water (mg of the carbon material per mL of water) under sonication. Afterwards, the pH of the dispersion is adjusted to 5.0 using NaOH. Then, the metal is reduced with an aqueous sodium borohydride solution with a molar relation $NaBH_4$ /metal precursor of 5, keeping the temperature below 18 °C and in presence of sonication. Finally, the resultant dispersion is filtered, washed with ultrapure water, and then dried overnight at 70 °C.

2.1.3 Reduction with ethylene glycol (EG method)

In this method, ethylene glycol is used as both solvent and reducing agent. Metal ions are reduced to form a metal colloid by receiving the electrons from the oxidation of ethylene glycol to glycolic acid [36]. This synthesis route requires of high pH in order to obtain small and uniform particles since glycolic acid is presented as glycolate anion, which is believed to act as a stabilizer by adsorbing the metal colloids in alkaline solution [40]. Briefly, the EG reduction method involves the following steps: first, the metal precursor is dissolved in ethylene glycol (16 mM) under sonication and the pH is adjusted to 11 adding 1 M NaOH solution. After that, the carbon support (4 mg of the carbon material per mL of ethylene glycol) is added and the mixture is refluxed at 195 °C for 2 h and subsequently quickly cooled in a cold water bath. Then, the pH is adjusted to 1 using HCl. Resultant catalyst is filtered, washed with ultrapure water and heated at 70 °C for 24 h.

2.2 Physicochemical characterization

Carbon-supported electrocatalysts prepared by the methods described above were characterized by different physicochemical techniques like scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

SEM micrographs were obtained using a Hitachi S-3400N microscope provided with an EDX analyzer Röntec XFlash Si(Li).

TEM micrographs were obtained using a JEOL-2000 FXII microscope equipped with a LaB6 gun or a Tecnai F30 (300 kV) equipped with a scanning transmission electron microscopy (STEM) module and a high-angle annular dark-field detector. The sizing of the samples was carried out from transmission electron micrographs using the

software Digital Micrograph by the observation of about 200 particles from different locations, while data were analyzed by means of the software OriginPro 9.0.

XRD patterns of the electrocatalysts were recorded using a Bruker AXS D8 Advance diffractometer with a θ - θ configuration and using Cu K α radiation ($\lambda = 0.15406$ nm). Scans were done at 1°min^{-1} for 2Θ values from 10° to 80° for all the samples. Crystallite sizes for metal or metal oxides nanoparticles of Pt, Cu, Fe, Ni and Co were calculated from adjusting the respective diffraction line (considering all the peaks) to a pseudo-Voigt function by means of the Pawley-LeBail method and refining the cell parameters, using the Scherrer's equation and the software TOPAS which allows a proper deconvolution of the signals associated to carbon and metal nanoparticles. The peak width was obtained from the integral breadth (IB) which is equivalent to the width of a rectangle with the same area and peak height than the studied peak assuming $K = 1$ [41].

TGA experiments were carried out on a thermogravimetric SETARAM Setsys Evolution under air atmosphere. The temperature was varied between room temperature and 950°C with a heating rate of $5^\circ \text{C min}^{-1}$.

2.3. Electrochemical characterization

2.3.1 Experimental set-up

Electrochemical measurements were performed at room temperature and atmospheric pressure in a conventional electrochemical cell of three electrodes: a working electrode (WE), a reference electrode (RE) and a counter electrode (CE, also denoted as auxiliary electrode). The electrochemical reaction of interest occurs at the surface of the WE. The RE presents a constant and known potential acting as a reference value for the measurements. Finally, the CE assures the electron balance. A

high surface area carbon rod was used as a CE, whereas an Ag/AgCl/3M KCl (0.21 V vs. reversible hydrogen electrode, RHE) electrode placed inside a Luggin capillary was employed as RE. Unless otherwise specified, all potentials in the text are referred to the Ag/AgCl/3M KCl electrode.

The WE was prepared depositing a thin-layer of the corresponding noble metal-free catalyst over the glassy carbon disk (7mm of diameter, SIGRADUR ® G). Carbon inks were prepared by mixing 2 mg of the respective carbon-supported electrocatalyst, 15 μ L of Nafion dispersion (5 wt. %, Aldrich) and 500 μ L of ultrapure water (Millipore Milli-Q system). The suspension was ultrasonicated for 40 min. An aliquot of 10 μ L of the suspension was pipetted onto the carbon disk and dried at room temperature resulting in a final load of 0.02 mg metal cm⁻² and 0.32 mg Nafion/mg catalyst. The potentiostat-galvanostat was an Autolab PGSTAT302 (Ecochemie). A gas bubbler completes the experimental setup.

2.3.2 Electrochemical measurements

The electrochemical behavior of the catalysts was studied by linear or cyclic voltammetry. Briefly, voltammetry consists on linearly sweeping the potential with time (i.e., the applied signal is a voltage ramp) and recording the current developed by the working electrode as a function of the applied potential. In linear voltammetry the voltage is scanned from a lower limit to an upper limit, whereas in the case of cyclic voltammetry the potential is cycled between two values, obtaining the corresponding linear (LV) or cyclic voltammograms (CV).

The experimental methodology consisted on the following steps: first, the WE was immersed into the electrolyte solution, 0.1 M NaHCO₃ (Merck, ACS $\geq$ 99 wt.%); pH = 8.4. N₂ was used to deaerate all solutions. This media was selected since most CO₂

reduction study has been conducted in close neutral electrolyte solutions. In this context, the hydrogen evolution reaction (HER), which occurs in aqueous electrolytes by cathodic polarization, is prevalent in acid solutions, while CO₂ forms bicarbonate and carbonate when it is purged through alkaline solutions decreasing the CO₂ reduction rate. 10 potential cycles between -0.8 and -1.6 V vs. Ag/AgCl (from -0.1 to -0.9 V vs. RHE) in 0.1 M NaHCO₃ solution deaerated with N₂ were recorded at 50 mV s⁻¹ in order to clean and activate the catalyst surface. For the Fe-based electrocatalysts, voltammograms were displayed from -0.8 to -1.6 V vs. Ag/AgCl to prevent overoxidation of the electrode surface. Then, a voltammogram was recorded at 10 mV s⁻¹ to study the electrochemical features of the catalysts in the working electrolyte. This voltammogram may be considered as a fingerprint of the material in the solution. After that, another aliquot of 10 µL of the catalyst ink was deposited and activated following the same procedure explained above, and CVs were recorded at cathodic potentials from -0.8 to -1.6 V vs. Ag/AgCl with the aim of evaluating the activity of the fresh electrodes toward the HER, which occurs as a competitive reaction during CO₂ reduction.

Finally, CO₂ was bubbled into the electrolyte for 30 min in order to obtain a CO₂ saturated 0.1 M NaHCO₃ solution leading to a pH decrease (from 8.4 in 0.1 M NaHCO₃ to 6.8 in the presence of CO₂). In this case, activation of the electrode was not necessary since it was the same used for HER experiments. Electrochemical measurements were carried out under CO₂ atmosphere to avoid its consumption during the tests. The electrolyte solution was removed before each measurement to avoid metal traces poisoning of the electrode surface during the experiments [42].

3. Results

3.1. Physicochemical characterization of the electrocatalysts

3.1.1. Metal catalysts prepared by the WI route

The physicochemical properties of 20 wt. % M/Vulcan catalysts (M = Cu, Fe, Co or Ni) prepared by the WI method were characterized by different analytical methods. In addition, a Pt/Vulcan catalyst was also used to establish a comparison. This last catalyst was prepared by the BH method since an agglomeration of large nanoparticles was obtained by the WI route due to the strong sintering of Pt during thermal treatment. However, the hydrogen reduction was necessary to obtain metal nanoparticles in the case of non-noble metals since reduction with borohydride or ethylene glycol resulted in the formation of metal oxide nanoparticles (see later section 3.1.2).

The catalysts metal loading was determined by EDX and TGA in air (Table 1). Several assumptions were considered to obtain the metal content by this last method. TGA were carried out under air atmosphere from room temperature to 950 °C. Thus, it was assumed that after these experiments, Fe, Co, Cu and Ni would be present in the highest oxidation state: Fe_2O_3 , Co_2O_3 , CuO , and NiO , respectively, which may lead to some uncertainty in the determination of the metal content due to the possible formation of an oxide distribution. In the case of Pt, this consideration was not taken into account since it was verified by XRD that TG analysis resulted in a superficial oxidation of the metal, and hence, the core remains metallic after oxidation. In addition, the ash content of the Vulcan used as support (with a value of 2.3 obtained also by TGA under the same conditions) was subtracted of the final result. As can be seen in Table 1, the metal content was similar to the nominal value of 20 % by both techniques for all catalysts.

Table 1. Metal content (obtained from EDX and TGA), average crystal size from XRD and mean particle size from TEM of M/Vulcan catalysts prepared by the WI route.

Sample	M wt.% EDX	M wt.% TGA	Crystal size (nm) XRD	Particle size (nm) TEM
Cu/Vulcan_WI	17.1	19.1	51.1	47.8 ($\sigma = 14.1$)
Fe/Vulcan_WI	21.0	19.2	43.7	25.7 ($\sigma = 11.5$)
Co/Vulcan_WI	21.3	18.8	16.6	13.7 ($\sigma = 5.2$)
Ni/Vulcan_WI	18.4	17.9	20.3	20.1 ($\sigma = 12.1$)
Pt/Vulcan_BH	18.9	18.5	4.4	2.6 ($\sigma = 0.6$)

The structural properties of M/Vulcan electrocatalysts were studied by XRD. Figure 1 shows the diffraction patterns obtained for all the samples. As can be seen, three diffraction peaks appeared in all these catalysts, which are ascribed to the (111), (200) and (220) planes of the corresponding metals, indicating that the active phase was deposited with a fcc structure, with the exception of Fe/Vulcan_WI where the planes (110) and (200) related to the formation of iron crystals with body centred cubic (bcc) structure were observed. In addition, a diffraction peak associated to the (311) plane of magnetite (Fe_3O_4) or its oxidized form maghemite (Fe_2O_3) was also displayed in this catalyst. A differentiation of maghemite and magnetite is not possible by XRD since both phases present the same structure. Finally, it is noticeable that the diffraction peak at around $2\theta = 25^\circ$, which is attributed to the graphite (002) contribution of the support, is also observed in the diffractograms. The mean crystallite sizes were calculated from adjusting the respective diffraction line to a pseudo-Voigt function, considering the IB as the peak width. The results are reported in Table 1. As can be seen, the electrocatalysts based on Cu and Fe presented higher crystallite sizes (ca. 51 and 44 nm, respectively), while lower values were obtained for Co/Vulcan_WI (ca. 17 nm) and Ni/Vulcan_WI (ca. 20 nm). On the other hand, Pt crystallite size was around 4 nm.

Figure 1. XRD patterns of Pt/Vulcan_BH and M/Vulcan_WI electrocatalysts.

SEM micrographs obtained from the interaction of secondary electrons (left images) and backscattered electrons (right images) showed a high dispersion of the active phase on the carbon support for all the electrocatalysts (Figure S1). STEM images provided more insight about the dispersion, size and morphology of metal particles.

Figure 2. STEM images and PSD of M/Vulcan catalysts prepared by the WI route: Cu/Vulcan_WI (a), Fe/Vulcan_WI (b), Co/Vulcan_WI (c) and Ni/Vulcan_WI (d).

A homogenous distribution of the metal on the carbon support was observed for the catalysts based on non-noble metals (Figure 2). However, the average particle size was larger in comparison to Pt/Vulcan_BH (with a mean diameter around 2-4 nm, see Figure S2), especially for Cu/Vulcan_WI, where particles of around 50 nm were mainly obtained, although larger grains (~ 200 nm) were also displayed (but they are not extended over the whole sample). This effect could be explained by the sintering of the metal particles during the reduction stage under H₂ atmosphere. On the other hand, wide PSDs were observed for M/Vulcan_WI catalysts. Co/Vulcan_WI exhibited the narrower distribution with an average value of around 14 nm. Additionally, average particle sizes of the different metals correlate quite well with the crystallite sizes obtained by XRD (see Table 1).

Remarkably, in the case of the Fe/Vulcan_WI catalyst, most of iron nanoparticles seemed to be covered with an oxide layer as can be better observed in Figure S3. STEM-EDX analysis through a selected nanoparticle corroborated that the relative content of iron was higher on the core of the particle. Thus, the metal Fe core is enclosed in an oxide shell. In agreement with the results obtained by XRD, the metallic Fe nanoparticles could be covered with a layer of maghemite and/or magnetite. In addition, some iron oxide hollow nanoparticles were also detected in this catalyst.

3.1.2. Cu and Fe catalysts prepared by different routes

Cu and Fe catalysts were synthesized by three different routes (BH, EG and WI methods) in order to obtain different catalytically active surface structures, which may modify the performance for CO₂ reduction. Cu was selected for this study due to its high efficiency for the formation of hydrocarbons and alcohols [3, 8, 43, 44], whereas electrodes based on Fe have also shown a high activity toward the CO₂ reduction

reaction [24, 26, 29]. It is important to note that scarce works in the bibliography are devoted to elucidate the effect of the preparation method on the physicochemical features of these materials [45].

In general, the metal content obtained by EDX and TGA was around 16-20% for the electrocatalysts prepared by the different synthesis routes (Table 2), indicating that BH and EG methods were also effective for the deposition of the desired metal amount.

Table 2. Metal content (obtained from EDX and TGA), average crystal size from XRD and mean particle size from TEM of Cu and Fe electrocatalysts prepared by different routes.

Sample	M wt.% EDX	M wt.% TGA	Crystal size (nm) XRD	Particle size (nm) TEM
Cu/Vulcan_WI	17.1	19.1	51.1	47.8 ($\sigma = 14.1$)
Cu/Vulcan_BH	17.6	17.8	6.9	400 (long) – 100 (wide)*
Cu/Vulcan_EG	16.5	16.3	30.4	≈ 20 -25*
Fe/Vulcan_WI	21.0	19.2	43.7	25.7 ($\sigma = 11.5$)
Fe/Vulcan_BH	15.6	17.0	-	≤ 5 *
Fe/Vulcan_EG	16.7	16.3	-	≤ 1 *

(*) A PSD was not obtained for these catalysts due to the irregular shape and the low definition of the nanoparticles.

The structural properties of Cu and Fe carbon-supported materials were studied by XRD. Figure 3 shows the diffraction patterns obtained for each metal by the different preparation methods. From the diffraction lines, metal crystallite sizes were obtained and the results are reported in Table 2. In the case of Cu, different oxidation states were obtained by the preparation methods (Figure 3a). When the WI route was used, three characteristic peaks appeared at $2\theta = 43.4$, 50.5 and 74.2° , which can be assigned to

(111), (200) and (220) planes of Cu, respectively, indicating that this metal was deposited with a fcc structure. On the other hand, by the EG and BH synthesis methods, the diffraction peaks associated to the copper oxides Cu_2O and CuO were found, indicating that copper was deposited in its oxidation states Cu(I) and Cu(II), respectively. In this context, Cu(I) is not stable in aqueous solution since it suffers disproportion to Cu and Cu (II). However, in the EG method, ethylene glycol is used as both solvent and reducing agent, and thus the disproportion of Cu(I) might not be favoured in this media. Finally, the average crystallite size was around 51 nm for Cu/Vulcan_WI, whereas catalysts prepared by the EG and BH methods exhibited lower values (30 and 7 nm, respectively).

Regarding the structural properties of Fe/Vulcan catalysts prepared by the different routes (Figure 3b), metallic iron with an average crystallite size of 44 nm was obtained for the catalyst synthesized by the WI method, whereas iron oxide nanoparticles, magnetite or maghemite, were obtained by BH and EG routes. For the later materials, calculation of the crystallite size was not possible due to the low resolution of the diffraction patterns. These results suggest that the values are below 2 nm, and consequently it cannot be characterized by XRD, and/or that part of the metal was deposited on the carbon material forming a stable but amorphous structure. Summarizing, WI route resulted in the deposition of metal Cu or Fe particles on the Vulcan support (as was already studied in the previous section 3.1.1), whereas BH and EG methods led to the formation of metal oxides.

Figure 3. XRD patterns of Cu/Vulcan (a) and Fe/Vulcan (b) electrocatalysts prepared by the different routes.

A good dispersion of the nanoparticles onto the carbon support was again observed by SEM (Figure S1 and Figure S4) for the Fe and Cu-based electrocatalysts with the exception of the Fe/Vulcan_BH where regions with a higher particle density were also evident (Figure S4c). In order to obtain a further insight about the distribution and size of metal and oxide nanoparticles STEM was used. Figure 4 shows the

micrographs obtained for Cu and Fe catalysts prepared by the BH and EG methods, while the results for Cu/Vulcan_WI and Fe/Vulcan_WI were already given before in Figure 2a and 2b, respectively (see previous section 3.1.1). Different shapes and sizes of nanoparticles were observed depending on the preparation method for Cu/Vulcan catalysts. Spherical particles of around 50 nm were obtained when copper was reduced under H₂ atmosphere (Figure 2a), while lower particle sizes with rather irregular shape were observed on Cu/Vulcan_EG, being the mean diameter around 20-25 nm (Figure 4b), although particles below 5 nm were also displayed. In contrast, the Cu/Vulcan_BH catalyst (Figure 4a), consists on flat, elongated nanoparticles up to 400 nm long and 100 nm wide, which contain small crystallites of around 7 nm, in correlation with the results obtained by XRD. These rod-like structures have been also obtained by other authors for CuO-based catalysts [46, 47].

When Fe was used as active phase, spherical nanoparticles with a range from 10 to 80 nm were obtained by the WI route (Figure 2b). Similarly, in the case of the Fe/Vulcan_BH (Figure 4c), a regular pavement of sponge-like particles lower than 5 nm was observed. Their shape is rather irregular and many edges are evidenced, probably due to their amorphous character. Finally, when EG was used as reducing agent a high dispersion of iron oxide nanoparticles was obtained (Figure 4d). EDX analysis confirmed the presence of Fe, O and C over the whole sample (see Figure S5). However, the size of the nanoparticles could not be clearly determined by STEM due to their low value (≤ 1 nm). This amorphous character and/or the small size of the Fe oxide particles obtained by the BH and EG methods hindered their characterization by XRD.

Figure 4. STEM images of Cu and Fe electrocatalysts prepared by the different routes: Cu/Vulcan_BH (a), Cu/Vulcan_EG (b) Fe/Vulcan_BH (c) and Fe/Vulcan_EG (d).

Finally, comparing the physicochemical properties of the catalysts prepared by the BH method (Fe/Vulcan_BH and Cu/Vulcan_BH) with those obtained for Pt/Vulcan_BH (section 3.1.1), Pt nanoparticles of around 3-4 nm were observed for Pt-based catalyst, while metal oxides with crystalline (CuO) and amorphous structure (magnetite or maghemite) were obtained for Cu/Vulcan_BH and Fe/Vulcan_BH, respectively.

3.2. Electrochemical measurements

3.2.1. Electrochemical behaviour in the working electrolyte

The electrochemical characterization of noble metal-free catalysts was performed in 0.1 M NaHCO₃ at room temperature and atmospheric pressure by cyclic voltammetry. At the beginning of the experiments, CVs were carried out at 0.01 V s⁻¹ in 0.1 M NaHCO₃ saturated with N₂ in order to study the electrochemical behaviour of the catalyst in the working solution (0.1 M NaHCO₃) which can be considered as blank voltammograms, that is to say specific fingerprints of the corresponding material in the working electrolyte. Different potential windows were selected for the catalysts according to the oxidation/reduction features of each metal.

Figure 5 displays the results for the metal-based electrocatalysts (i.e. those obtained by the method of wetness impregnation and reduction with hydrogen at 650 °C). The electrochemical behaviour at anodic potentials of non-noble metals in neutral and alkaline solution is rather complex as it comprises several reactions involving the formation of different oxide and hydroxide films by passivation [48-52]. Moreover, in moderate alkaline solutions containing NaHCO₃/Na₂CO₃, the HCO₃⁻ and CO₃²⁻ ions may promote either the corrosion or the protection of the metals [49, 50]. Several authors have studied the electrochemical behaviour of Cu, Co, Fe and Ni electrodes in

alkaline solutions [48-56]. However, pronounced discrepancies exist between these studies probably due to differences in the electrode pretreatment, solution composition and sample structure, as well as the potential windows used in the experiments and the solution stirring.

Figure 5. CVs for M/Vulcan catalysts prepared by the WI route in 0.1 M NaHCO_3 ($v = 10 \text{ mV s}^{-1}$).

Different anodic-cathodic branches, which are associated to oxidation (positive currents in the voltammograms in Figure 5) or reduction processes (negative currents) respectively, were obtained for the M/Vulcan catalysts depending on the active phase:

(i) The Cu-based electrocatalyst exhibited two anodic signals at -0.13 (peak I) and 0.10 V (peak II) which may be associated to the oxidation of Cu to Cu(I) and to Cu(II), respectively [48, 49]. Accordingly, two cathodic peaks were obtained at -0.18 and -0.51 V corresponding to the reduction of CuO and Cu_2O , respectively [48, 49, 57].

(ii) Several anodic peaks appeared on Fe/Vulcan_WI: a main oxidation signal at -0.62 V (peak II) with a shoulder at -0.80 V (peak I) and different anodic currents at more positive potentials (denoted as III). According to literature peak I could be assigned to the surface formation of $\text{Fe}(\text{OH})_2$ species, while peak II results from the growth of the anodic layer and the simultaneous chemical dissolution of Fe, which appears to be assisted by bicarbonate ions [50, 53, 58]. The anodic currents at more positive potentials (III) are related to the precipitation of the FeCO_3 -containing anodic layer leading to the formation of Fe(III) species. Correspondingly, the cathodic processes at -0.62 and -1.11 V occur by the reduction of Fe(III) and Fe(II) species, respectively.

(iii) In the case of Co/Vulcan, a main anodic peak is observed at -0.30 V (peak II) and two satellite humps appear one at ca -0.54 V (peak I) and another one at -0.07 V (peak III). According to the literature, features I and II are associated to the formation of Co(II) species, such as CoO or $\text{Co}(\text{OH})_2$, while at potentials above peak III the formation of Co(III) becomes possible and the passivation film consists of the duplex $\text{CoO}/\text{Co}_3\text{O}_4$ [51, 54, 55, 59]. During the negative-going potential excursion, a defined cathodic peak at ca -0.95 V appears which can be related with the reduction of Co(III) and Co(II)-containing films.

(iv) Finally, in the case of Ni/Vulcan_WI, the anodic signal at -0.25 V (peak I) is attributed to the oxidation of Ni, which leads to the enrichment of Ni^{2+} in the surface of the electrode and subsequent formation of $\text{Ni}(\text{OH})_2$. At more positive potentials, the passivation of Ni to $\text{Ni}(\text{OH})_2$ will be favoured, leading to the dissolution of the $\text{Ni}(\text{OH})_2$ film at 0.20 V (peak II) [52, 60].

Similarly, a typical voltammogram in slightly alkaline media was obtained for the Pt catalyst [61, 62] (Figure S6) with an anodic peak at potentials above 0.2 V related

to the formation of platinum oxides and their corresponding reduction in the negative scan at around -0.2 V.

3.2.2. Electrochemical activity toward hydrogen evolution reaction

The HER takes place as a competitive reaction during CO₂ conversion by the water reduction. However, the presence of adsorbed hydrogen onto the catalyst surface is a requirement for CO₂ activation and hydrogenation. Consequently, an effective catalyst for CO₂ reduction should be able to suppress the HER so that all the adsorbed hydrogen will be consumed only by CO₂ reduction and the subsequent hydrogenation to reduced species. Pt electrodes have been widely studied due to their great ability to adsorb hydrogen (low hydrogen overpotential) [6, 7]. However, only traces of reduction products were generally detected and hydrogen was the main product [12, 63]. In contrast, hydrocarbons, alcohols and formic acid have been obtained on non-noble metals with medium/low hydrogen overpotentials, such as Cu [3, 8, 64]. Thus, the study of the electrochemical activity for HER is essential to obtain a deeper insight of the electrochemical reduction of CO₂.

The cathodic faradic currents at potentials below -1.2 V (-0.7 V for Ni/Vulcan_WI) in Figure 5 are associated to the hydrogen formation by water reduction. In order to study in detail the performance of the electrocatalysts toward the HER, current curves were recorded at more negative potentials (from -0.8 to -1.6 V vs. Ag/AgCl) in 0.1 M NaHCO₃ preventing the oxidation of the electrocatalysts, which may lead to a modification of the catalyst surface, and consequently, of the electrochemical activity, or even to dissolution of the active phase. To note that the voltammogram for Fe/Vulcan_WI was recorded from -1.0 to -1.6 V since this catalyst presents already oxidation at -0.8 V (see Figure 5, red curve). Under these conditions (in

absence of CO₂) the faradic cathodic currents in these potential regions are only associated to the HER. Figure 6 displays a comparison of the results recorded for the electrocatalysts prepared by the WI route. The voltammograms obtained on the Pt/Vulcan catalyst and the carbonaceous support Vulcan are also registered for comparison.

Figure 6. LVs at cathodic potentials for M/Vulcan catalysts prepared by the WI route, Pt/Vulcan BH and Vulcan in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$).

First of all, it has to be noted that the formation of hydrogen is shifted to more positive potentials and the cathodic current increased for all the electrocatalysts in comparison to the carbonaceous support Vulcan, showing that the metal phase was effectively deposited on the carbon material.

Different activity toward HER of the electrocatalysts is evident from comparison of the faradic currents at negative potentials. As expected, the HER is enhanced on the Pt electrode starting the hydrogen formation at potentials below -0.6 V. Regarding non-noble metal based catalysts, the catalytic activity increases following the sequence: Cu

$\text{Fe} \approx \text{Co} < \text{Ni}$, being nickel the most active material for the formation of H_2 . Other authors have also reported a high electrocatalytic activity toward the HER on nickel and its alloys [65-67]. In contrast, copper showed the lowest activity for HER. It is important to remark that the experimental conditions involved for the preparation of metal nanoparticles were not optimized for each metal, resulting in different particle size distributions which may affect the activity for H_2 formation. In this context, Cu/Vulcan_WI exhibited the highest average particle size (c.a. 50 nm) and the lowest activity was displayed. Thus, the catalytic activity toward the HER strongly depends on the used material, the surface metallic arrangement and the particle size distribution.

In order to study in detail about the influence of the oxidation state on the performance for this reaction, the electrocatalysts of Fe and Cu prepared by the different routes (WI, BH and EG methods) were also tested and the results are given in Figure 7.

Figure 7. LVs at cathodic potentials for Cu and Fe catalysts in 0.1 M NaHCO_3 ($\nu = 10 \text{ mV s}^{-1}$) prepared by different methods.

In the case of copper-based catalysts, the metallic electrode (Cu/Vulcan_WI) exhibited a better performance toward the HER, with a higher cathodic current for this reaction. In this context, larger crystallites sizes ($\approx 50 \text{ nm}$) were obtained for Cu/Vulcan_WI in comparison to the copper oxide catalysts prepared by the EG and BH

methods, with values of 30 (Cu/Vulcan_EG) and 7 nm (Cu/Vulcan_BH), respectively. In addition, the former catalyst presented larger particles (~ 200 nm) probably due to the sintering during the reduction stage under H_2 atmosphere. As a consequence, a lower efficiency could be expected on the former surface. However, this catalyst presented the highest cathodic current which may be explained by differences in the oxidation state of the catalysts, being the hydrogen formation favored on the metallic catalyst, in comparison to the catalysts based on metal oxides (Cu_2O for Cu/Vulcan_EG and CuO for Cu/Vulcan_BH). In contrast, similar cathodic currents were obtained for all Fe-based electrocatalysts. As was characterized by XRD and STEM, Fe/Vulcan_BH and Fe/Vulcan_EG consist on small and amorphous particles of maghemite or magnetite, while Fe/Vulcan_WI presented core metal particles covered by crystalline oxides (maghemite and magnetite), which could lead to a similar activity for this reaction. Thus, although amorphous metal oxides were obtained with EG and BH methods, similar efficiencies were exhibited for the hydrogen formation, showing that these synthesis routes were also effective for the preparation of active Fe electrocatalysts for HER. Other authors have obtained a good performance toward the HER on amorphous metals [68-70]. So, like copper-based catalysts it seems that the oxidation state is again a key parameter in the electrochemical performance toward HER.

3.2.3. Electrochemical activity toward the CO_2 reduction reaction

Finally, electrocatalysts were tested for the CO_2 electroreduction process. With this aim, current curves at the most negative potentials were also monitored in the base electrolyte after saturation with CO_2 for 30 minutes. In order to take into account the differences of pHs between the electrolytes (8.4 in the solution saturated with N_2 and 6.8 in the presence of CO_2), voltammograms were represented versus the RHE by using the equation 1:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.21 + 0.059 \text{ pH} \quad (1)$$

which involves a shift to more positive potentials of 59 mV for each pH unit (8.4 in 0.1 M NaHCO₃ or 6.8 after CO₂ saturation) according to the Nernst equation.

LVs for the noble metal-free catalysts prepared by the WI route are displayed in Figure 8. In absence of CO₂ (black curves in Figure 8) the faradic currents at potentials below -0.4 V vs. RHE are associated to the hydrogen formation, while that the signals developed in the base electrolyte after CO₂ saturation (red curves in Figure 8) are related to both reactions; the HER and the CO₂ reduction.

Figure 8. LVs for M/Vulcan catalysts prepared by the WI route in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$). Black curves: N₂ saturated solution. Red curves: CO₂ saturated solution. Blue curves: CO₂ saturated solution after 10 cycles at 50 mVs^{-1} in the presence of CO₂.

All the electrocatalysts behaved similarly: at potentials below -0.4 V vs. RHE,

the cathodic current was decreased in presence of CO₂, which is attributed to the inhibition of HER due to the adsorption of species derived from CO₂ reduction (CO_{2,red}) such as CO and/or formates [3, 8, 52, 56, 60, 64]. These results show that CO₂ is effectively reduced to adsorbed species on all the catalyst surfaces. The cathodic current is progressively inhibited by cycling at 50 mV s⁻¹ in the CO₂-saturated base electrolyte solution, reaching a constant value after 10 scans (see Figure 8, blue curves). Comparing the current at -0.9 vs. RHE in presence and absence of CO₂ (black and blue curves in Figure 8), an inhibition of the current around 36 % was developed for the Co and Fe-based electrocatalysts, respectively, while a higher value (around 45 %) was obtained on Cu/Vulcan_WI and Ni/Vulcan_WI, which could be associated to a higher adsorption of (CO_{2,red}) intermediates on the last catalysts. In this context, the presence of adsorbates from CO₂ reduction has been already reported by other authors in bulk copper and nickel electrodes under different conditions [3, 8, 52, 56, 60, 64]. However, the adsorption of (CO_{2,red}) species is not favored on electrodes based on massive Co or Fe at room conditions, obtaining H₂ as the main product by the reduction of water [1, 11, 12]. However, all these studies were performed involving bulk electrodes. A recent work (unpublished results) [71] found an inhibition of the current in the presence of CO₂ at potentials below - 0.8 V vs. RHE in 0.1 M NaHCO₃ using the carbon support Vulcan as electrode, which is explained by the (CO_{2,red}) adsorption on the free-metal surface. Thus, the use of carbon-supported catalysts could enhance the formation of adsorbates.

A similar trend was obtained on the Pt/Vulcan electrocatalyst with an evident inhibition of the current at potentials below -0.0 V vs. RHE (see Figure 9, right). Consequently, an anodic peak appeared at 0.7 V vs. RHE associated to the oxidation of these adsorbates [5, 63, 72, 73]. Remarkably, the oxidation of these adsorbed species is

already evident when cycling in the potential range from -0.1 to 1.6 V vs. RHE (-0.8 and 0.9 V vs. Ag/AgCl) (Figure 9, left).

Figure 9. CVs for Pt/Vulcan_BH catalyst in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$): from -0.1 to 1.6 V vs. RHE (left) and from -0.7 to 1.6 V vs. RHE (right). Black curves: N₂ saturated solution. Red curves: CO₂ saturated solution.

The influence of the oxidation state of Cu and Fe catalysts on the activity toward the CO₂ electroreduction was also evaluated. Similarly to the results obtained by the metallic electrocatalysts (prepared by the WI route), a lower activity was obtained at negative potentials in a CO₂-saturated solution for Cu and Fe oxide-based catalysts (obtained by the EG and BH methods). Figure 10 shows the results obtained for two selected electrocatalysts (those synthesized by reduction with BH). Interestingly, a strong current decrease was observed on copper oxides (Cu/Vulcan_BH: 74% and Cu/Vulcan_EG: 84 %) in comparison to the metal-based catalyst (Cu/Vulcan_WI: 46%), which may be explained by a higher formation of adsorbates on the former electrocatalysts. Other authors have reported a high performance toward CO₂ reduction on copper oxide electrodes in comparison to Cu [19-23]. In contrast, Fe-oxide electrocatalysts showed a similar behavior to Fe/Vulcan_WI (with a current inhibition around 36%), which is explained by their similar surface structures based on

maghemite/magnetite oxides even on the reduced catalyst (Fe/Vulcan_WI).

Figure 10. LVs for Cu and Fe catalysts prepared by the BH route in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$). Black curves: N₂ saturated solution. Red curves: CO₂ saturated solution. Blue curves: CO₂ saturated solution after 10 cycles at 50 mV s^{-1} in the presence of CO₂.

Thus, the use of carbon-supported catalysts seems to promote the CO₂ reduction to adsorbed species for all the catalysts (regardless of the active phase and the oxidation state). These adsorbates may be further reduced forming volatile compounds, that is (CO_{2,red}) species may act as intermediate to high-value products (such as methanol or formic acid). Interestingly, promising results have been already obtained using gas diffusion electrodes based on Fe/Vulcan_EG in acid media (0.5M H₂SO₄ 0.5 M) [29, 63]. Formic acid was detected as major product by on line differential electrochemical mass spectrometry, while H₂ (by water reduction) was mainly obtained on a Pt/Vulcan electrode. These results are explained by an irreversible adsorption of (CO_{2, red}) species on the Pt electrode (as was shown before, Figure 9), which act as self-poisoning inhibiting further reduction. In contrast, adsorbates formed on Fe/Vulcan_EG may be easier converted to other volatile products. Additionally, a recent work has shown that the Fe-based electrode could be also effective for CO₂ reduction in gas phase [63].

4. Conclusions

The electrochemical behavior for CO₂ reduction of carbon-supported catalysts based on non-noble metals (Cu, Fe, Co and Ni) was investigated in 0.1 M NaHCO₃ by voltammetry. In addition, Fe and Cu oxide-based electrocatalysts were also studied. Metal catalysts were synthesized by the WI method, while oxides were obtained by reduction of metal precursors with BH and EG with a crystalline structure in the case of Cu (CuO for Cu/Vulcan_BH and Cu₂O for Cu/Vulcan_EG) or amorphous oxides (magnetite or maghemite) for Fe.

Metallic electrocatalysts displayed different activities toward the H₂ evolution reaction (which occurs during CO₂ reduction in aqueous electrolytes), being Ni and Cu the most and less active, respectively. In addition, an improved efficiency for H₂ formation was shown for the Cu⁰ (Cu/Vulcan_WI) catalyst in comparison to copper oxides (Cu/Vulcan_BH and Cu/Vulcan_EG), while Fe-based catalysts presented similar performances. Despite of these noticeable differences, a significant decrease in the current developed in the H₂ evolution region was obtained in a CO₂-saturated 0.1 M NaHCO₃ solution for all (metal and oxide-based) electrocatalysts, which demonstrates the adsorption of species derived from CO₂ reduction at all electrode surfaces. Interestingly, the formation of adsorbates has been shown for the first time on Co and Fe-based catalysts operating in 0.1 M NaHCO₃ under room conditions showing that the use of a carbon support may enhance the (CO_{2,red}) adsorption rate on these metals. Finally, a strong current decrease, and consequently, a higher (CO_{2,red}) adsorption, was observed on copper-oxides (75-85 %) in comparison to the metal catalyst (46 %).

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4.4. REFERENCES

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Tables

Table 1. Metal content (obtained from EDX and TGA), average crystal size from XRD and mean particle size from TEM of M/Vulcan catalysts prepared by the WI route.

Sample	M wt.% EDX	M wt.% TGA	Crystal size (nm) XRD	Particle size (nm) TEM
Cu/Vulcan_WI	17.1	19.1	51.1	47.8 ($\sigma = 14.1$)
Fe/Vulcan_WI	21.0	19.2	43.7	25.7 ($\sigma = 11.5$)
Co/Vulcan_WI	21.3	18.8	16.6	13.7 ($\sigma = 5.2$)
Ni/Vulcan_WI	18.4	17.9	20.3	20.1 ($\sigma = 12.1$)
Pt/Vulcan_BH	18.9	18.5	4.4	2.6 ($\sigma = 0.6$)

Table 2. Metal content (obtained from EDX and TGA), average crystal size from XRD and mean particle size from TEM of Cu and Fe electrocatalysts prepared by different routes.

Sample	M wt.% EDX	M wt.% TGA	Crystal size (nm) XRD	Particle size (nm) TEM
Cu/Vulcan_WI	17.1	19.1	51.1	47.8 ($\sigma = 14.1$)
Cu/Vulcan_BH	17.6	17.8	6.9	400 (long) – 100 (wide)*
Cu/Vulcan_EG	16.5	16.3	30.4	$\approx 20\text{-}25^*$
Fe/Vulcan_WI	21.0	19.2	43.7	25.7 ($\sigma = 11.5$)
Fe/Vulcan_BH	15.6	17.0	-	$\leq 5^*$
Fe/Vulcan_EG	16.7	16.3	-	$\leq 1^*$

(*) A PSD was not obtained for these catalysts due to the irregular shape and the low definition of the nanoparticles.

Figure Captions

Figure 1. XRD patterns of Pt/Vulcan_BH and M/Vulcan_WI electrocatalysts.

Figure 2. STEM images and PSD of M/Vulcan catalysts prepared by the WI route: Cu/Vulcan_WI (a), Fe/Vulcan_WI (b), Co/Vulcan_WI (c) and Ni/Vulcan_WI (d).

Figure 3. XRD patterns of Cu/Vulcan (a) and Fe/Vulcan (b) electrocatalysts prepared by the different routes.

Figure 4. STEM images of Cu and Fe electrocatalysts prepared by the different routes: Cu/Vulcan_BH (a), Cu/Vulcan_EG (b) Fe/Vulcan_BH (c) and Fe/Vulcan_EG (d).

Figure 5. CVs for M/Vulcan catalysts prepared by the WI route in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$).

Figure 6. LVs at cathodic potentials for M/Vulcan catalysts prepared by the WI route, Pt/Vulcan BH and Vulcan in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$).

Figure 7. LVs at cathodic potentials for Cu and Fe catalysts in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$) prepared by different methods.

Figure 8. LVs for M/Vulcan catalysts prepared by the WI route in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$). Black curves: N₂ saturated solution. Red curves: CO₂ saturated solution. Blue curves: CO₂ saturated solution after 10 cycles at 50 mVs⁻¹ in the presence of CO₂.

Figure 9. CVs for Pt/Vulcan_BH catalyst in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$): from -0.1 to 1.6 V vs. RHE (left) and from -0.7 to 1.6 V vs. RHE (right). Black curves: N₂ saturated solution. Red curves: CO₂ saturated solution.

Figure 10. LVs for Cu and Fe catalysts prepared by the BH route in 0.1 M NaHCO₃ ($v = 10 \text{ mV s}^{-1}$). Black curves: N₂ saturated solution. Red curves: CO₂ saturated solution. Blue curves: CO₂ saturated solution after 10 cycles at 50 mVs⁻¹ in the presence of CO₂.