A Gas-phase Electrochemical Reactor for Carbon Dioxide Reduction back to Liquid Fuels

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We report on the development of a novel electrochemical reactor working in gas phase for recycling CO_2 back to liquid fuels. Operating in gas phase (without any solvent) has many benefits with respect to the conventional aqueous slurry reactors: no problems of CO_2 solubility, easy and less costly recovery of the products, etc. The reaction mechanism of CO_2 reduction is also quite different in gas phase and longer chains of products (oxygenates and hydrocarbons) can be obtained in comparison with C1 products in liquid phase.

Particularly, competition between CO_2 reduction process and water electrolysis (with generation of hydrogen) at the cathode side was investigated and discussed in this contribution. The understanding of these competitive phenomena is very significant in order to minimize H_2 formation and increase the process efficiency.

The electrocatalysts prepared for the cathode are based on nanostructured carbons (multiwalled carbon nanotubes) doped with suitable metal nanoparticles (such as Pt, Fe, Co and Cu). The skill of developing advanced nanostructured electrodes by modulating their properties during the synthesis allowed to improve the process performance, enhancing the productivity and also tuning the selectivity towards higher chain hydrocarbons and other chemicals.

The CO_2 reduction to liquid fuels by solar energy represents an attractive solution which may contribute to the alternative use of clean and renewable sources to cope with the depletion of fossil fuels. The target is to develop a sort of "artificial leaf" which may collect the solar energy as the nature does, by capturing directly CO_2 and converting it back to fuels.

1. Introduction

Carbon dioxide scenario has witnessed important changes in recent years, evolving towards a new idea of CO_2 that is now considered as a resource and a business opportunity rather than a waste with a high impact on the environment and a cost of disposal (Genovese et al., 2013c).

In this perspective, photo-electrocatalytic reduction of CO_2 back to liquid fuels by using a renewable energy resource (sunlight) represents a highly attractive solution to i) close the cycle of CO_2 production/consumption, ii) diminish the CO_2 level in the environment and iii) reduce fossil fuel consumption (Centi et al., 2011). That is one of the great challenges for the use of clean and renewable energy allowing to develop a sort of "artificial leaf" capable of converting CO_2 by collecting solar energy in the same way as the nature does (Bensaid et al., 2012). Moreover, increasing amounts of low-cost and relatively pure CO_2 will be soon available from current and planned plants for carbon sequestration and storage (CSS) (Ampelli et al., 2011b). Currently, the research goals are centred to the need of developing not just efficient, but also cost-effective and robust technologies and materials to be used in solar energy applications (Natali Sora et al., 2013; Ampelli et al., 2012b).

The process of CO_2 reduction to liquid fuels is considered as one of the artificial photosynthesis processes. Photosynthesis by plants, as known, consists of two main reactions: in the light reaction the water is decomposed to H_2 and O_2 under sunlight irradiation and in the dark reaction adsorbed CO_2 is hydrogenated by H_2 and fixed as carbohydrates. To mimic what plants do during the natural photosynthesis, the artificial devices should be

designed to reduce CO_2, but it is a common practice to consider artificial photosynthesis as a simplified process of using sunlight to break water into H_2 and O_2 (Hoffmann et al., 2011).

Our approach is based on a novel photo-electrocatalytic (PEC) reactor working in gas phase (Ampelli et al., 2012a) which consists of: i) a photo-anode formed by a TiO_2 thin film characterized by a highly ordered nanostructure where O_2, protons and electrons are produced by water splitting (Passalacqua et al., 2012); ii) an electro-cathode composed of metal nanoparticles supported on C-based substrates with a configuration similar to a gas-diffusion membrane (GDM), in which CO_2 is reduced using the protons and electrons coming from the anode side and passing through a proton selective membrane (Nafion®) and a wire, respectively (Ampelli et al., 2011a). The design of the PEC reactor takes advantage of fuel cell technology and the electrode materials are assembled together like a MEA (membrane electrode assembly) in a fuel cell (Ampelli et al., 2009).

Gas phase operation is very attractive because allows to solve some critical issues related to aqueous slurry reactors, which are used in the most of the electrocatalytic processes of CO_2 reduction reported in literature (Varghese et al., 2009): there is no solvent at the cathode side and therefore no need to recover the products from a liquid phase, no problems of CO_2 solubility, etc. (Ampelli et al., 2013). Moreover in gas phase the reaction mechanism is quite different and longer chains of products may be obtained; in the liquid phase instead the main products obtained are C1 (or at most C2) hydrocarbons or oxygenates. The target is, in fact, the formation of liquid fuels with C>1 because they are easier to transport and store, preserving the large investments made in the current energy and chemical infrastructures. Therefore, CO_2 electrocatalytic conversion has the potential to become a key pillar of the sustainable and resource-efficient production of chemicals and energy from renewables (Genovese et al., 2013a).

The aim of this work is to investigate the feasibility of the electrocatalytic gas-phase conversion of CO_2 to hydrocarbons and oxygenates using C-based nanostructured electrocatalysts (doped with Pt and also with not noble metal nanoparticles, i.e. Fe) as part of a photoelectrocatalytic (PEC) device which, by using sunlight and water, is able to convert CO_2 back to liquid fuels (Ampelli et al., 2010). The nature of the electrocatalyst plays a significant role to control the process yield and selectivity allowing to form long C-chain liquid fuels. We started from commercial multiwalled carbon nanotubes (CNTs) and then modified them by using advanced chemical and thermal techniques. The CNTs are suitable materials to prepare such kinds of electrodes for their high electron conductivity, flexibility and possibility of easy tuning of properties during the synthesis (Centi and Perathoner, 2011). The influence of: the kind of CNTs, deposition of metal nanoparticles, different operating conditions and various other aspects were evaluated in order to improve the productivity and selectivity.

In particular, the mechanism of H_2 formation as side reaction in the electrocatalytic process was in depth investigated. This aspect has poorly been studied in literature but is of paramount importance to enhance the overall process efficiency (Genovese et al., 2013b). The influence of the presence of a co-metal (Co, Cu) together with Fe in the CNT electrocatalyst was also discussed.

2. Experimental

Commercial multiwalled carbon nanotubes with inner diameter in the range of 50-100 nm were purchased from Applied Science (CNT, Pyrograph®-III, PR24) and used as starting materials. The CNTs were heat-treated in inert gas at 700 °C (PS), 1500 °C (LHT) or 3000 °C (HHT) to remove the polyaromatic carbon layer covering their outer surface thus increasing the graphitization level and inherent conductivity. Then the samples were chemically treated in boiling nitric acid (HNO_3 65 wt. %) for 10 h to functionalize the surface of the CNTs creating a variety of oxygen groups. Finally they were washed with distilled water until neutral pH and dried at 80 °C overnight. 10 wt. % metal nanoparticles were deposited on CNTs by incipient wetness impregnation using an ethanolic solution containing the metal precursor(s): $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$. After drying at 60 °C for 24 h, the samples were annealed for 2 h at 350 °C and reduced in H_2 at 400 °C for 2 h. The total amount of metals (10 wt. %) was chosen in order to have an amount comparable to the metal loading in the electrocatalysts for PEM fuel cells which corresponds to a small metal loading in the final catalyst (about 0.5 mg/cm^2).

This procedure leads to metal nanoparticles with average size between 10-20 nm for Fe or other non-noble metals, such as Co and Cu, while smaller particles average size, between 1-3 nm, were observed for noble metals such as Pt. However by adopting this procedure, the deposition of metal precursors occurs both on the external and internal walls of the CNTs (Lago et al., 1995). In order to realize a selective filling of the metal nanoparticles only inside the channels of the CNTs, the samples may be washed after the first step of impregnation with water to dissolve the film on the external walls of CNTs but maintaining unchanged the solution in the inner channels (Tessonier et al., 2009.).

X-ray diffraction analyses were performed for bimetallic catalysts in order to confirm the alloy formation by using a Philips X-Pert diffractometer equipped with a Ni β-filtered Cu-Kα radiation at 40 kV and 30 mA. Data were collected at a scanning rate of 0.025° s-1 in a 2θ range from 5 to 100°.

The electrodes were prepared by using methods which are easy, cost-effective and potentially scalable for a large use but an appropriate assembly of the electrode materials is fundamental for a good contact and adherence of the different layers. The electrodes are in the form of a gas diffusion membrane (GDM) consisting of a gas diffusion layer (GDL) and a Nafion® membrane, which are assembled together to allow the electrical contact and diffusion of gas phase to the electrocatalyst. To prepare the GDL, an ethanol suspension of metal-doped CNTs was deposited on a commercial substrate (SIGRACET® GDL 24BC, supplied by SGL Group). After drying, the final GDM working electrode was assembled by hot-pressing joining the GDL on a proton selective membrane (Nafion® 115, by Sigma Aldrich) at 80 atm and 130 °C for 90 s. The active phase (CNTs) is located between the GDL at direct contact with CO_2 gaseous stream and the Nafion® membrane. A 1 cm^2 electrode was used.

The experiments were carried out in a homemade continuous hemi-cell at 60 °C and for simplicity the photo-generated current was simulated by applying a constant small bias through the cell to supply the electrons necessary for the CO_2 reduction process. In this configuration the photo-anode was replaced by a compartment filled with a liquid electrolyte solution as source of protons; a Pt wire (as counter-electrode) and a saturated Ag/AgCl electrode (as reference electrode) were located in this part of the reactor. Figure 1 shows some pictures of the electrochemical reactor. In the final PEC system, no electric potential and electrolyte will be needed, as the protons and electrons will be produced by water photo-electrolysis (activated by sunlight).

A potentiostat/galvanostat (Amel mod. 2049A) is used to supply the current and monitor the potential between the working and counter/reference electrodes. Experiments were conducted galvanostatically, inverting after 1 h the current polarity to improve desorption of the products from the working electrode. Tests were also performed applying a constant potential (-1.5 V) and reading the generated current (potentiostatic mode), to quantify the total electrons needed from the photo-anode in the full PEC device.

The analysis of the products of reaction, collected in a cold trap, was performed by a gas-chromatograph equipped with a mass detector (Thermo Scientific GC Trace 1310 - ISQ MS).
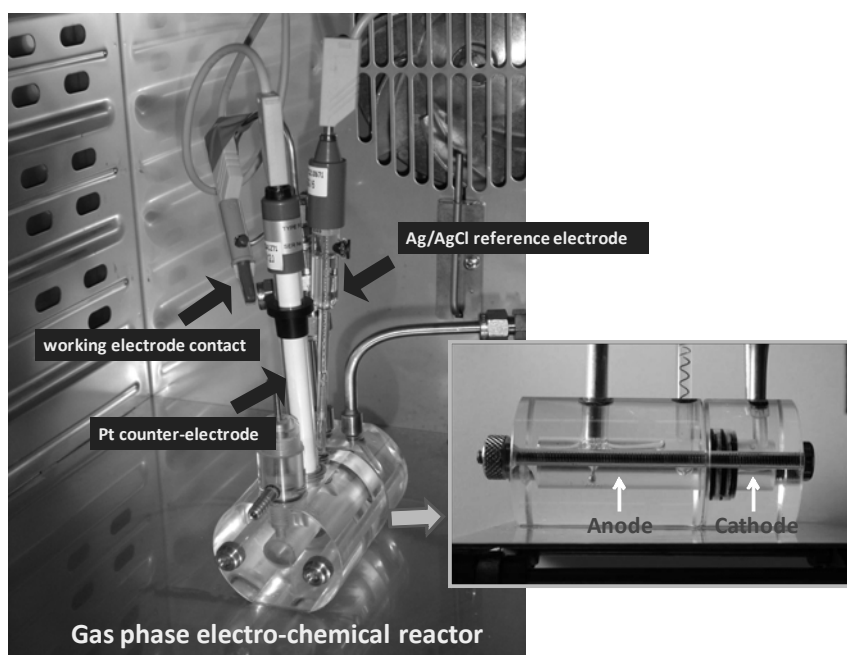

Figure 1: Photos of the electrochemical reactor working in gas phase for the process of CO_2 reduction to liquid fuels.

3. Results and discussion

The electrochemical reduction of CO_2 in solvent-less conditions involves multi electron processes which can lead to a large variety of products ranging from CO to various oxygenates such as alcohols, aldehydes, and carboxylic acid by a complex multistep mechanism that is probably quite different in comparison with the liquid phase conditions (largely investigated in literature) in which mainly C1 products are obtained. The key aspect in order to improve the overall efficiency is not only the preparation of a proper C-based nanostructured electrode (doped with suitable metals) but also the capability to assemble the electrode materials to form a multilayered composite to guarantee good proton mobility and electron conductivity. The reactor was in fact designed taking into account these engineering aspects which are usually the critical factors limiting these kinds of cells.

Another important issue, poorly investigated, in such a kind of electrocatalytic cell configuration is the presence of water which is in both the hemi-cells. The process, in fact, consists of two half-reactions which, for simplicity, we report only for the production of isopropanol, as follows:

$$9H_2O = 4.5O_2 + 18H^+ + 18e^- \tag{1}$$

$$3CO_2 + 18e^- + 18H^+ = C_3H_8OH + 5H_2O \tag{2}$$

The half-reaction in Eq. 1 occurs at the anode side (photo-anode or simulated-anode in our current PEC system) and refers to the water oxidation to give O_2 while protons and electrons migrate to the other side through the Nafion® membrane and the external circuit, respectively. At the cathode side protons and electrons combine together with CO_2 on the electrocatalyst layer to give the formation of hydrocarbons and oxygenates products (Eq. 2). It is to notice that water is present in both the hemi-cells; in particular a small amount of water arrives at the cathode side due to permeability of the Nafion® membrane which is in direct contact with the anode aqueous solution; moreover water is also a product of the half-reaction of Eq. 1 and we are able to collect it in the cold trap together with the other liquid fuels. Thus the presence of water in the electrocatalytic system is unavoidable. Unfortunately the standard reduction potential of H_2O to form H_2 is considerably lower than the standard reduction potential of CO_2 to form $CO_2^{\bullet-}$ (Indrakanti et al., 2009). Therefore, from a thermodynamic point of view it should generally be more favourable to reduce H_2O than CO_2, but so far this aspect has not still been investigated. In order to minimize the competitive side reaction of water splitting, we analysed the outlet gas phase stream from the reactor to determine the H_2 generation rate.
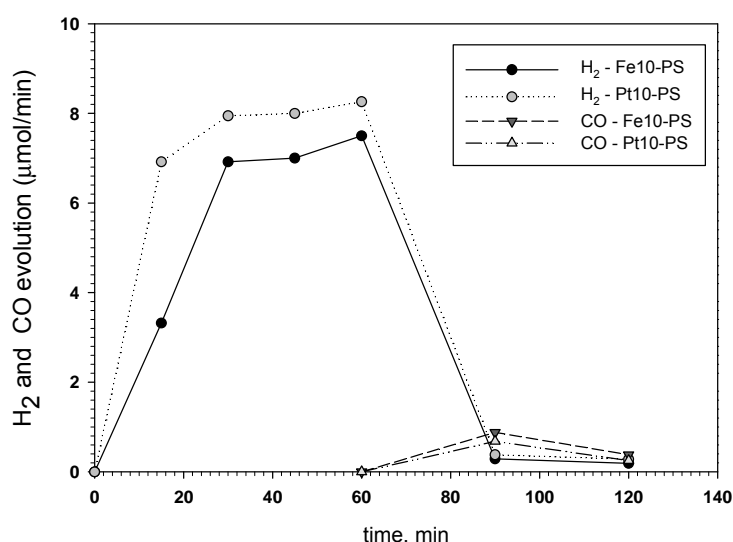

Figure 2: H_2 and CO production rates for Fe/CNT and Pt/CNT electrocatalysts treated at 700 °C (PS) (The amount of metal is 10 wt.%)

Generally the deposition of noble metal nanoparticles, and particularly Pt, plays a beneficial effect on the efficiency of a water splitting process. It has been found that the presence of small size Pt particles (5-10 nm) facilitates the kinetics of H_2 formation which desorbs to the gas phase, because the Pt nanoparticles act as electron attractors and sites of proton adsorption/desorption (Ampelli et al., 2012b). Although with some differences (i.e. photo-catalytic processes of water dissociation are catalysed by semiconductors, usually titania) the deposition of 10 % Pt nanoparticles on CNT (sample Pt10-PS) increased H_2 generation with respect to not noble metal (Fe10-PS) as it is shown in Figure 2. On the contrary, carbon monoxide, which is the main intermediate in liquid fuel generation, was produced in higher concentrations for Fe than Pt. It is to notice that during the first step of the electrocatalytic process (1 h), no CO was detected in the outlet gas stream, probably because it remains chemisorbed on the surface of the electrocatalyst. The inversion of the applied current facilitates the desorption of CO, which was thus detected in the outlet gas stream, as well as of the liquid fuels which were collected in the cold trap.

Another aspect to take into account is the power supply to be furnished in order to simulate the solar energy. The quantity of the electric current depends not only on the efficiency of the electrocatalyst but also on the reactor design. In fact, to perform a (photo)electrochemical process a power (or sunlight) supply is needed to make the process thermodynamically favourable, but also the over potential effects should be taken into account and these phenomena strongly depend on the reactor configuration and electrode assembling. Initially we measured an average open circuit potential of ~0.6 V; thus the current to be furnished to the simulated PEC system was at least 10 mA (due to the ohmic losses of the cell). We also performed testing experiments at 20 mA and results are reported in Figures 3 and 4 for Fe and Pt on CNT (PS) respectively.
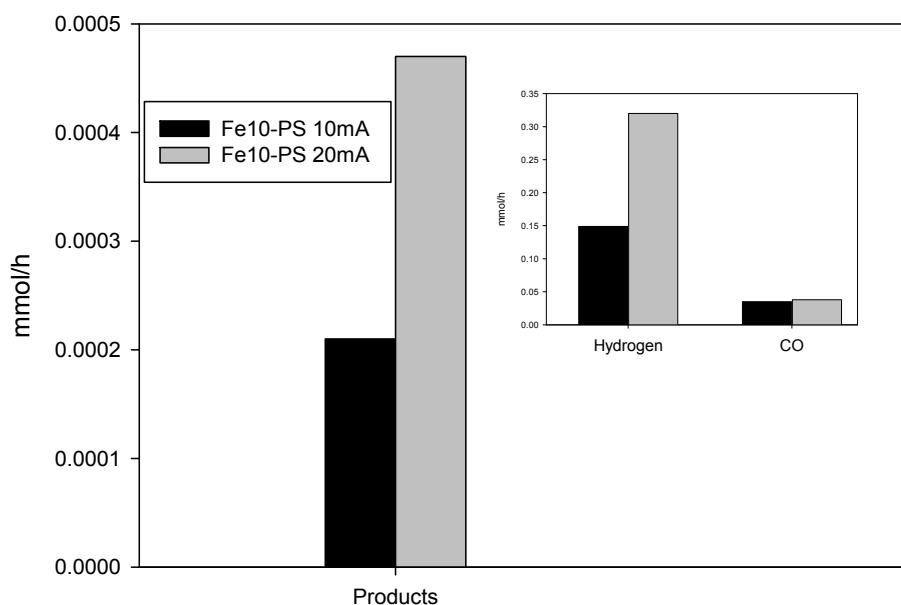

Figure 3: Effect of the current density on the productivity to liquid fuels for a Fe/CNT electrocatalyst treated at 700 °C (PS); insert: H_2 and CO production.
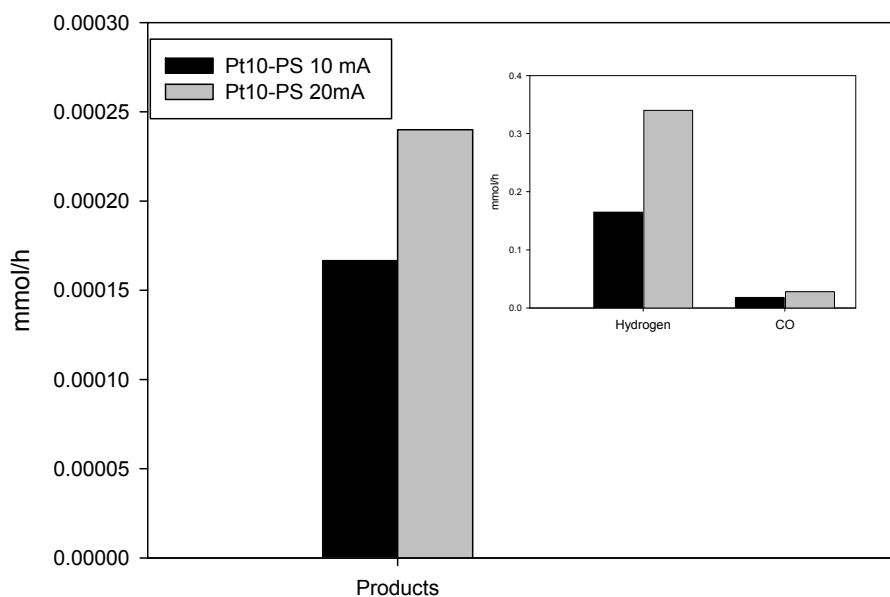
Figure 4: Effect of the current density on the productivity to liquid fuels for a Pt/CNT electrocatalyst treated at 700 °C (PS) insert: H_2 and CO production.

The electric current furnished to the system was almost totally converted into chemical energy (with conversion higher than 90 %). There is a good agreement of the productivity data (total amount of liquid products and hydrogen) and a linear increase from 10 to 20 mA was observed, with the exception of carbon monoxide which remains almost as constant, especially in the case of Fe. Referring to the reaction mechanism, a possible explanation is that probably the formation of C-C bonds is the rate determining step of the whole CO_2 reduction process, but more specific investigations are needed to confirm this hypothesis. Other experiments were performed increasing the applied current to the cell above 20 mA (until 40 mA) and a worsening of the productivity was observed, although slightly increasing the fraction of heavier products ($\geq$C2). It is to notice that higher chain hydrocarbons (C3-C8) were detected in all the testing experiments, but here we have limited our analysis to the fractions C1-C3.

Furthermore, the nature of carbon-based substrate influences the catalytic efficiency; the carbon support, in fact, does not only play a role in the dispersion of the nanoparticles, but also has other functions important in determining the electrocatalytic performances, determining the effectiveness of transport of electrons and protons to the metal nanoparticles. Therefore, it is important to analyse how the characteristics of carbon support influence the performances of the electrocatalyst.

Reported in Table 1 is the comparison of the total productivity to liquid fuels in CO_2 electroreduction between Fe nanoparticles supported on CNTs and two of the most used conductive carbon supports for the preparation of the electrocatalysts in PEM fuel cells, Vulcan XC-72 and Ketjen black. The amount of Fe and the method of preparation are the same in all these samples. The behaviour is very similar between Fe on Ketjen black and Vulcan XC-72, instead the use of CNTs as support allows about to double the productivity in liquid fuels.

The catalytic effects of CNTs generally depend on the presence of surface functional groups that better anchor the metal nanoparticles (which are the actual catalytic sites) and may strongly modify their intrinsic reactivity. Moreover their particular morphology improves some important properties in electrochemical applications, such as electron conductivity, high surface area, robustness and chemical inertness.

Table 1: Productivity to CO_2 electroreduction products and C1-C3 selectivity for Fe10-PS (treated at 700 °C), Fe10-Ketjen and Fe10-Vulcan electrocatalysts. Reaction conditions: 60°C, constant current density (10 mA).

|	Productivity, mmol/h	Selectivity, %		
	Hydrocarbon/Oxygenates	*C1*	*C2*	*C3*
Fe10-PS	$2.1*10^{-4}$	30	55	14
Fe10-Ketjen	$1.3*10^{-4}$	64	34	2
Fe10-Vulcan	$1.2*10^{-4}$	82	16	2

The heat-treatment is very useful to remove the polyaromatic carbon layer covering the outer surface of CNTs and increase the graphitization level and inherent conductivity. In order to investigate this aspect, preliminary experiments were carried out comparing the CNT samples thermally treated at different temperatures (PS, LHT and HHT). The CNTs contain the same loading of Fe or Pt (about 10 wt. % with respect to CNTs, ~0.5 mg/cm^2 of the electrode surface). Table 2 shows the results of the experiments for Fe and Pt electrocatalysts on different CNTs. It is evident that CNTs-PS samples give the best performances in CO_2 reduction process in terms of hydrocarbon and oxygenate productivity.

Thus the increase of graphitization of the external surface of CNT by annealing at higher temperatures (from 700 up to 3000 °C) produces worse results, because probably it is more difficult the functionalization by chemical treatment, and consequently the efficient dispersion of metals to produce small nanoparticles. Evidently the presence of defects on the C-based substrate, that act as anchoring sites for the stabilization of the metal nanoparticles, is of great importance to perform the electrocatalytic process and 700 °C was the optimal temperature to guarantee both a good level of graphitization (high electron conductivity) and the right presence of defects. For this reason, we preferred to carry out all the experimental tests (previously reported) by using CNTs-PS samples (treated at 700 °C) as C-based support.

Table 2: Productivity for Fe/CNT and Pt/CNT electrocatalysts treated at 700 °C (PS), 1500 °C (LHT) and 3000 °C (HHT). (The amount of metal is 10 wt. %; current density 20mA, T=60°C).

	Productivity, mmol/h		
Electrocatalysts	Products (mmol/h)	H_2 (mmol/h)	CO (mmol/h)
Fe10-PS	$4.7*10^{-4}$	0.32	0.038
Fe10-LHT	$1.4*10^{-4}$	0.32	0.018
Fe10-HHT	$2.0*10^{-4}$	0.30	0.032
Pt10-PS	$2.4*10^{-4}$	0.34	0.028
Pt10-LHT	$6.8*10^{-5}$	0.36	0.015
Pt10-HHT	$2.5*10^{-5}$	0.34	0.020

In order to enhance further the productivity in the electrocatalytic reduction of CO_2, the use of bimetallic metal nanoparticles on CNTs treated at 700°C (PS) were also investigated. The contemporary deposition of two or more metals on CNTs may lead either to the formation of an alloy or alternatively the metals remain distinct in more phases. It is known that the behaviour of alloys is often very different from those of the single metals, especially when the particles are small at the nanoscale (2-15 nm).
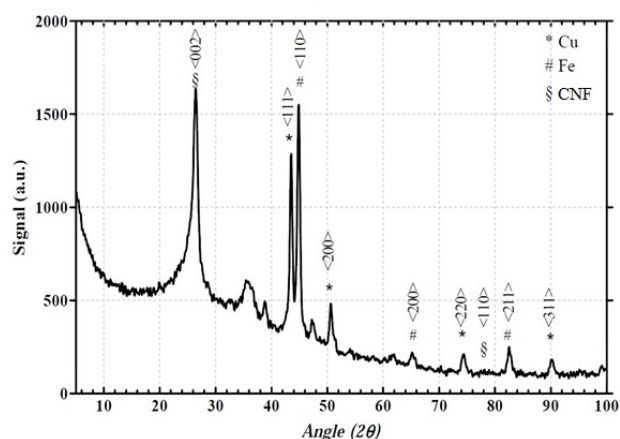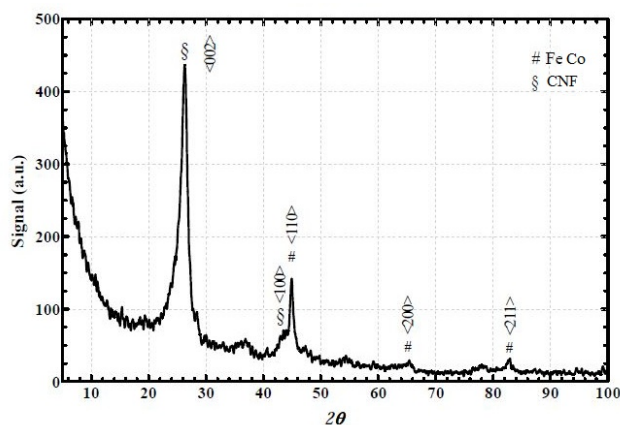
Figure 5: XRD patterns for a) Fe5Cu5-PS and b) Fe5Co5-PS samples.

We tried to prepare two Fe alloys adding the precursor salt of Co (or Cu) during the incipient wetness impregnation. The effective formation of the alloy was verified by XRD analysis. XRD patterns confirmed the formation of Fe-Co alloy *bcc*-faces, while Fe-Cu remains in two separate phases as confirmed by literature data that indicate that metallic Cu and Fe are immiscible (He et al., 2012) and Fe can only exist on the surface of the reduced Cu in form of small particles. Figure 5 shows the XRD images for the Fe5Cu5-PS and Fe5Co5-PS electrocatalysts. Reported in Table 3 are the results obtained in terms of productivity and selectivity to liquid fuels for CNT-PS samples prepared by the deposition of two metal (Fe-Cu and Fe-Co). The data of Fe10-PS were also reported for a comparison. The products which we are able to detect are methane, methanol, formaldehyde, formic acid, acetaldehyde, ethanol, acetic acid, isopropanol, acetone but also butanol, aromatics and other hydrocarbons in the range of C4-C8 were detected. However we focused our attention on liquid fuels in C1-C3 range to have an idea of the actual formation of at least one or two C-C bonds. The presence of Fe-Co alloy nanoparticles on CNT surface improves the selectivity to C3 products with respect to the sample with only Fe, while the Cu nanoparticles in bimetallic phase with Fe give mainly C1 and C2 products. However Fe5Cu5-PS sample allowed to obtain a higher productivity and less CO formation.

The interpretation of these results is not very easy confirming that the reaction mechanism is rather complex. Each doping metal, such as Fe, Co, Cu and Fe-Co alloy, plays a specific role to catalyze the single steps of CO_2 reduction process, which may be referred mainly to i) CO formation and ii) C-C bond formation. We may conclude asserting that the presence of Fe and Co in alloy facilitates C-C bond formation while the combination of Fe with Cu has a promoting effect on increasing the productivity.

Table 3: Productivity to liquid fuels and C1-C3 selectivity for bimetallic catalysts in comparison with Fe10-PS (the total amount of metals is 10 wt. %; current density 10mA).

	Productivity, mmol/h	Selectivity, %		
	Hydrocarbon/Oxygenates	*C1*	*C2*	*C3*
Fe10-PS	$2.1*10^{-4}$	30	55	14
Fe5Co5-PS	$2.2*10^{-4}$	19	65	16
Fe5Cu5-PS	$4.0*10^{-4}$	33	64	2

4. Conclusions

In this work we developed a novel electrochemical device for the CO_2 reduction back to liquid fuels working in gas phase and we optimized the electro-cathode part by using C-based materials doped with Pt or Fe and other non noble metal nanoparticles (Co and Cu) as co-catalysts. The CNTs are very suited materials to develop advanced nano-structured electrodes, for the realization of solar devices which may mimic the natural photosynthesis.

Many different aspects influence the process of CO_2 reduction: i) the need to have a good mobility of both the electrons and active hydrogen species on the metal nanoparticles, ii) the efficient contact with the proton selective membrane and iii) the possibility of introducing specific active sites in CNTs.

In particular we here discussed on the competitive reaction of H_2 generation by water electrolysis, which has to be minimized to give way to the formation of liquid fuels. Unfortunately, the presence of water is unavoidable because it is a co-product of the cathode half-reaction and also permeates through the Nafion® membrane. However, the use of Fe instead of Pt allowed to reduce the H_2 formation enhancing the productivity of liquid fuels. Experiments at different power supplies (10-20 mA) and with not noble metal (Fe, Cu and/or Co) electrocatalysts (deposited as small nano-particles in the CNT substrates) were also reported with the aim to clarify some aspects of the reaction mechanism of CO_2 reduction. The formation of C-C bonds is probably the rate determining step of the whole CO_2 reduction process, but more specific investigations are needed to confirm this hypothesis.

Moreover, a study on the nature of reaction intermediates could further improve the understanding of the mechanism which is probably quite different in gas than liquid phase. It could resemble a Fischer-Tropsch reaction but the operating conditions are quite different, i.e. the process occurs at lower temperatures (60 °C).

It is to remark that this electrode design for the electrocatalytic reduction of CO_2 has been developed not only for an easier recovery of the reaction products, but also to be coupled with a photoanode able to generate the protons/electrons necessary to sustain the CO_2 reduction process. In a photo-electrochemical (PEC) solar cell, the protons should diffuse through a proton-conductive membrane (such as Nafion®) and a conventional metal foil electrode is not suitable for this application. As a result, a GDM-type electrode is fundamental for a good assembling in a PEC device. Also the photo-anode characteristics have to be suited for this coupling, and the use of a nanostructured photo-active materials may allow a fast transport of protons to the membrane and at the same time a fast collection of the photogenerated electrons (Ampelli et al., 2008). However, the actual implementation of a PEC solar cell is still a long way off and both the electro- and photo-materials must be improved in terms of performance, robustness and cost. All these aspects may take advantages of the large diffusion of PEM fuel cells, since they show several analogies with the PEC cells.

Finally, the electrocatalytic conversion of gaseous streams of CO_2 back to liquid fuels by using noble metal-free electrodes represents a valuable opportunity to introduce renewable energy into the existing energy and chemical infrastructure, having these products a higher energy density and easier transport/storage than competing solutions (i.e. hydrogen) and allowing the reuse of CO_2 to contribute in closing carbon dioxide cycle responsible for greenhouse effect. Although there will be necessary a long time of research before a real application, the possibility to develop a PEC device able to convert CO_2, water and sunlight back to liquid fuels by using not expensive materials, is now an attractive prospective but placed on real basis.

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