Berenguer, R.; Marco-Lozar, JP.; Quijada, C.; Cazorla-Amoros, D.; Morallón, E. (2012). A comparison between oxidation of activated carbon by electrochemical and chemical treatments. Carbon. 50(3):1123-1134. doi:10.1016/j.carbon.2011.10.025

A comparison between oxidation of activated carbon by electrochemical and chemical treatments

R. Berenguer[a], J.P. Marco-Lozar[b], C. Quijada[c], D. Cazorla-Amorós[b] and E. Morallón[a]

[a]Departamento de Química Física and Instituto Universitario de Materiales. Universidad de Alicante. Apartado 99. E-03080 Alicante. Spain

[b]Departamento de Química Inorgánica and Instituto Universitario de Materiales. Universidad de Alicante. Apartado 99. E-03080 Alicante. Spain

[c]Departamento de Ingeniería Textil y Papelera, Universitat Politècnica de València. Pza Ferrándiz y Carbonell, E-03801 Alcoy (Alicante). Spain

Abstract

The anodic oxidation of a granular activated carbon (GAC) in NaCl solution has been studied. The influence of the electrocatalyst-anode material, applied current and time of treatment on both the surface chemistry and porous texture properties of the GAC has been analyzed. For comparison purposes, the same GAC has been treated with three of the classical chemical oxidants: HNO_3, H_2O_2 and $(NH_4)_2S_2O_8$ at different concentrations and for different times. Results show that the anodic treatment in NaCl causes a remarkable oxidation of the AC without modifying significantly its textural properties. TPD profiles and the linear dependence of the amount of CO- and CO_2-evolution against the oxidation level denotes that surface oxygen groups of similar nature and composition are formed anodically, regardless of the anode material. The achieved oxidation degree depends on the different ability of each anode for the electrochemical generation of highly oxidizing chlorine species, and it increases progressively with the applied current and the time of treatment. In general, for similar treatment times, the anodic treatment in

NaCl can produce oxidation degrees much higher than the chemical treatment with $(NH_4)_2S_2O_8$, which has been found to be the most oxidative chemical studied in this work.

*Corresponding author: Tel: +34-965909590. Fax: +34-965903537. E-mail address: morallon@ua.es (E. Morallón)

1. Introduction

The practical use and applications of activated carbons (ACs) in many industrial fields and technologies are based on their outstanding physicochemical properties, especially the surface area, the porous texture and the surface chemistry. In particular, the relevance of surface oxygen groups (SOGs) in the performance of carbon materials is known for more than 20 years [1-5]. The presence of SOGs on the graphene sheets or edges of carbon materials results in their destabilization, altering their acid-base and electron-donor/-acceptor properties [6,7] and modifying their hydrophobic character [8], conductivity [9], capacitance [9,10], etc. Moreover, upon tailoring surface complexes, affinity towards a wide variety of organic and inorganic compounds can increase and, hence, their performance in the removal/adsorption of some pollutants and in the recovery of metals can be enhanced [2]. In addition, SOGs act as anchoring sites for other functional molecules, which act as ligands, catalysts, or reactants in many important reactions [6]. They can also facilitate the incorporation of other materials, such as metallic or oxide nanoparticles, polymers, etc. [11,12], introducing or remarkably improving some properties.

Considering the huge influence of surface chemistry in the performance of carbon materials, methods allowing the control of both the nature and concentration of surface functional groups for specific applications would be of crucial importance. In general, the different AC properties mainly depend on the precursor nature and the synthesis route, but they can also be modified by a suitable post-treatment step. Although textural properties can be modified by thermal post-treatments, they are usually set by an adequate choice of the activation procedure. On the contrary, post-treatments are mainly used to modify the nature and concentration of SOGs.

Regarding the surface chemistry, post-treatments of as-received commercial AC or carbonaceous materials after activation consist of oxidation and/or reduction treatments in gas or liquid phase. The various AC modification techniques and their effects on AC properties have been the subject of intensive research [10,13-23]. The most used techniques for surface chemistry modification have been: (i) heating (500-1000ºC) under inert atmosphere [13-15], to selectively remove some of these functions, and (ii) the chemical post-treatment in liquid phase, using oxidants such as HNO_3, H_2O_2, $(NH_4)_2S_2O_8$ [13-19], to increase the concentration of SOGs. Other methods using oxidizing gases (O_2, O_3, Cl_2, etc.) [19-22] or oxygen plasma [23] have been also introduced.

However, in spite of being widely studied and applied, conventional chemical and thermal post-treatment methods are not suitable enough for controlling and modifying easily and selectively the surface chemistry of carbon materials. This could be due not only to the more complex experimental system and handling derived from using gases, harmful agents and/or high temperatures, but also, to the fact that neither the oxidizing power of a given oxidative agent nor the extent of oxidation reactions can be easily controlled and modulated. As a consequence, and unlike the advanced state of the art on optimization and tailoring of the porous structure of carbon materials [24], it is necessary to carry out much more exhaustive and detailed research on methods and tools for a higher control of the concentration and nature of SOGs in carbon materials.

The electrochemical method [25-32] has emerged as a promising technique for the modification of the surface chemistry of carbon materials in aqueous and organic solvents, because it presents several advantages when compared to conventional methods: mainly, (i) the treatment can be immediately interrupted and (ii) can be run at room temperature and atmospheric pressure; (iii) the reaction conditions can be very precisely reproduced; and (iv) oxidation and reduction processes are more selective and easily controlled by means of the proper setting of the applied current or electrode potential.

The electrochemical modification of a commercially-available granular AC has been recently studied in our research group. The influence of different electrochemical variables, such as the electrode polarity (anodic or cathodic), the applied current and the type of electrolyte was analyzed in detail [30]. In particular, it was observed that the anodic treatment in NaCl results in a high surface oxidation degree, which could be comparable to that of a traditional chemical oxidation. Nevertheless, the efficiency and performance of the different modification methods cannot be directly compared to each other if the modified carbon materials are different. Comparisons are necessary not only to demonstrate the real feasibility of new alternative methods but also to determine the suitability of a given AC modification method for the control of surface chemistry for specific applications.

In the literature on surface chemistry modification, some contributions on the comparison of different modification methods for the same AC carbon material can be found [12,14,17-20], but little work on comparison including the electrochemical oxidation technique has been reported to date [25-27]. Barton et al. [27] used activated carbons whereas the other authors [25,28] used conductive carbon materials. Shao et al. [26] studied the electrochemical oxidation of carbon black and carbon nanotubes in sulphuric acid in similar conditions than those encountered in low temperature fuel cells in order to analyze the stability of the carbon materials as support of the electrocatalysts. Instead, Barton et al. [27] estimated the anodic oxidation degree of a granular AC in a 0.5 M K_2SO_4 solution, at two constant currents and during different periods of time. It was found that a controlled formation of low levels of oxidation can be reached by the anodic process, but very long periods of time are necessary to achieve levels of surface oxidation comparable to those produced by chemical oxidation.

In order to further study new approaches on tailoring the surface chemistry of carbon materials, this work presents a comparative study between the treatments of the same granular AC material by conventional chemical modifications in liquid phase and through anodic oxidation in NaCl, this latter being the most oxidizing electrolyte among the various electrolytes tested by our group [30]. The influence of the applied current, the anode nature and time, in the case of the electrochemical method, and the effect of oxidant concentration or oxidation time, in the chemical one, on both the surface chemistry and textural properties of the AC have been analyzed. The comparison is based on the concentration of groups introduced after the modification treatment, the kinetics of the processes and the control of oxidation degree.

2. Experimental

2.1. Electrochemical oxidation of activated carbon.

The electrochemical modification of a commercial granular activated carbon (GAC) has been carried out anodically in a divided filter-press electrochemical cell. The detailed experimental conditions for a typical electrochemical modification process have been previously described [30]. Briefly, 2 g of the original washed GAC were galvanostatically treated at 0.2, 0.5, and 1.0 A for 3 h, in a flowing 2 wt% NaCl solution (200 cm^3), with 4 different anodes: Ti/SnO_2-Sb-Pt, Ti/RuO_2, Ti/Co_3O_4 and Ti/Pt, prepared by the conventional thermal decomposition method [34-36]. A steel electrode was used as the cathode and the area of all electrodes was 20 cm^2. For the analysis of time influence, Ti/RuO_2 was selected as the anode and experiments were performed for 1, 3 and 5 h.

For the preparation of the electrolyte solution, distilled water and analytical grade sodium chloride (Merck) were used. The commercial GAC studied in this work was provided by Waterlink Suctliffe Carbons (207A, $pH_{PZC} = 9$, Mesh: 12 × 20) and it is referred to as W.

The anodically modified AC samples will be referred to in the text as a compound name including the letter W, referring to the AC supplier (Waterlink); the simplified name of the employed anode: SnO_2, RuO_2, Co_3O_4 or Pt; the letter a to denote an anodic treatment; a number indicating the applied constant current (0.2; 0.5 or 1.0 A) and the abbreviation of Cl^-, referring to NaCl electrolyte solution. In the case of the study on time influence, the nomenclature also includes the number of hours of the experiment (1h, 3h or 5h). For example, the label $WSnO_2a0.2Cl^-$ (3h) refers to a GAC sample supplied by Waterlink, that was subjected to anodic treatment at 0.2 A in 2 wt% NaCl electrolyte by using an SnO_2-type anode for a total electrolysis time of 3 hours.

2.2. Chemical oxidation of activated carbon.

Chemical treatments of GAC were carried out in ground glass stoppered flasks, under magnetic stirring, with three oxidizing agents: HNO_3, H_2O_2 and $(NH_4)_2S_2O_8$. The ratio of carbon mass (g) to solution volume (mL) was always 1/10. In the case of nitric acid, carbon samples were put in contact with differently concentrated solutions: 23, 35 and 65 % at room temperature for 2 h. Oxidation with hydrogen peroxide was also performed with three different concentrations: 10, 20 and 33 %. In this case, however, solutions were boiled and the contact time was extended until total evaporation. For the third chemical reagent, a $(NH_4)_2S_2O_8$-saturated 1 M H_2SO_4 solution was employed (solubility in water at 20 ºC is 620 g/L) for: 2, 5 and 24 h. The oxidative chemicals and experimental conditions have been chosen in this way because they have been found to be some of the most commonly used in the literature on chemical oxidation of carbon materials [14-19].

The nomenclature employed for the chemically-modified samples involves the letter referring to the commercial AC (W); the letters N, H or S indicating the used oxidizing agent (HNO_3, H_2O_2 and $(NH_4)_2S_2O_8$, respectively); and finally, a number related to the concentration or the time of treatment (23%, 35% or 65% for HNO_3; 10%, 20% or 33% for H_2O_2; and 2h, 5h or 24h for $(NH_4)_2S_2O_8$).

2.3. Characterization of the activated carbon.

After the electrochemical and chemical oxidation experiments, and prior to their characterization, the AC samples were washed by soaking (24h) into successive portions of distilled water until constant pH was reached. Next, AC samples were filtered and dried at 110 °C overnight.

2.3.1. Porous texture characterization

The porous texture of all samples was determined by physical adsorption of gases (N_2 at -196 ºC and CO_2 at 0 ºC) using an automatic adsorption system (Autosorb-6, Quantrachrome Corporation) after sample out-gassing at 250 C under vacuum for 4 h. Nitrogen adsorption at -196 ºC has been used for determining the total volume of micropores ($V_{DR}(N_2)$) (pore size smaller than 2 nm), applying the Dubinin–Radushkevich (DR) equation, and for determining the specific surface area by the BET equation (S_{BET}). CO_2 adsorption at 0 ºC has been used to assess the narrowest micropores ($V_{DR}(CO_2)$) (pore size smaller than around 0.7 nm), also by application of the Dubinin–Radushkevich theory [37-39].

2.3.2. Surface chemistry characterization

The characterization of SOGs present in AC has been done by Temperature Programmed Desorption (TPD) experiments, using a DSC–TGA equipment (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, MSC 200). In these experiments, about 20 mg of the sample were heated up to 950 °C (heating rate 20 °C/min) under a helium flow rate of 100 mL/min.

3. Results and Discussion

3.1. Influence of applied current and anode material in the anodic oxidation of AC in NaCl

Figure 1 shows the CO_2 and CO TPD profiles obtained for AC samples treated anodically in 2 wt% NaCl at different applied current for 3 h, with different anodes, and those obtained for the untreated (original) AC sample. Table 1 summarizes the quantification of the CO and CO_2 evolved in these TPD experiments, the CO/CO_2 ratios and the total oxygen content (O), which has been calculated from the evolved CO and CO_2. Table 1 also shows quantification data for AC samples treated anodically for 1 and 5 h using a Ti/RuO_2 anode. The corresponding TPD profiles are shown in Fig. 2.

The characterization of the surface chemistry of the original AC (W) shows a low concentration of SOGs (Table 1), particularly of the most acidic ones, such as carboxylic and phenolic groups, which decompose at lower temperatures (see TPD profiles in Figure 1). These chemical features are in agreement with the basicity (pH_{PZC} = 9) of this carbon material, in which the basic character of graphitic basal planes may predominate.

As shown in Figures 1-2 and Table 1, the anodic treatment in NaCl with the different tested anodes remarkably increases the amount of both the CO_2- and the CO-evolving surface groups. As a result, the total surface oxygen amount (O) increases and therefore, the original GAC is oxidized to a considerable extent. Moreover, an increase in the applied current induces an increase in the oxidation degree of the activated carbons in all the current range investigated, regardless of the anode nature. As it has been previously proposed [30], the observed oxidation of the AC may arise from a combination of two processes: i) a direct anodic oxidation of the carbon particles owing to the positive potential reached at the anode and ii) an indirect oxidation process by electrogenerated chlorine species. It is well known that the electrochemical oxidation of chloride ions yields a series of highly oxidizing chlorine species such as free chlorine, hypochlorous acid and hypochlorite ions according to the following reactions [40,41]:

Anode surface: $2Cl^- \rightarrow Cl_2 + 2e^-$ (1)

Bulk solution: $Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^-$ (2)

$HClO \rightarrow H^+ + ClO^-$ (3)

These reactions have been reported to dominate over the oxidation of water via intermediate adsorbed hydroxyl radicals on Ti/Pt, [42], Ti/PbO_2 [43], Ti/IrO_2 [44], and Ti-based DSA anodes made of mixed transition metal oxides [40,41] in NaCl solutions. In accordance with the literature data we will assume that the second mechanism is the preferred one for the oxidation of AC samples in this work.

The CO_2 and CO profiles of GAC samples anodically-treated with different anodes and at different currents or electrolysis time (Figures 1-2) are similar in shape, suggesting that, although different in concentration, the SOGs introduced onto the GAC after the electrochemical treatment in NaCl are of the same nature for all anode materials. Nevertheless, there are some distinct features that should be noted regarding the evolution of the CO_2 peak associated with the most stable lactone groups. A slight to negligible increase in this type of groups is observed upon increasing current in electrolysis performed with Ti/RuO_2 and Ti/Pt anodes. On the contrary, the lactone peak decreases when the electrochemical treatment is done at Ti/Co_3O_4 anodes. Finally, the GAC sample treated at a SnO_2-based anode shows a general increase in all the acidic groups, especially carboxylic acid and lactone groups, and a lowering in the concentration of the latter at the highest electrolysis current.

The origin of the observed differences in the amount of surface oxygen groups and the TPD profiles are maybe due to the different electrode kinetics for the chloride electro-oxidation. Then, a more detailed analysis of individual contribution from specific surface oxygen groups in relation to the electrode used, could give a more accurate picture of the oxidation of the carbon surface. This kind of analysis is currently under preparation where deconvolution of the TPD profiles according to the procedure described by other authors will be used [45].

Figure 3 plots the increase in the amount of CO- and CO_2-type surface oxygen groups with respect to the pristine AC versus the increase in the total amount of oxygen loaded on the carbon surface for both the electrochemical and chemical treatments. Figure 3a shows that the increments in the amount of both CO- and CO_2-evolving groups grow linearly with the total oxygen incorporated on the carbon surface by anodic oxidation. Data points from electrolyses at different electrodes and input currents or treatment times (Table 1) fit fairly well to the same straight line. This linear dependence further supports our view that the characteristics of surface oxygen functionalities created by anodic treatment are not governed by the anode material, but they stem from the particular oxidation mechanism involving electrogenerated oxidizing species.

In fact, TPD profiles for AC oxidized anodically in H_2SO_4 medium (cf. Fig.2b, Ref 30) appear rather different than those in Figs 1-2 and the corresponding data points in Fig.3a do not follow the same trend than those in NaCl medium. The linear variation exhibited in Fig 3a indicates that the surface oxide concentration grows in a uniform fashion in NaCl electrolyte, i.e., groups desorbing as CO and groups desorbing as CO_2 grow at constant rate as the oxidation level increases, regardless of the anode material. This is probably a consequence of the fact that the electrochemical oxidation in NaCl electrolyte is mainly due to an indirect oxidation process through electrogenerated active chlorine species.

Unlike results reported by Barton and coworkers [27], the straight line in Fig 3a does not intercept the origin. Consequently, the $\Delta CO/\Delta CO_2$ ratio should change with the increasing oxidation level, instead of remaining constant. Parameters from linear fits in Fig 3a were used to predict $\Delta CO/\Delta CO_2$ ratios in order to realize their variation with the increasing oxidation degree. Simulated $\Delta CO/\Delta CO_2$ ratios are plotted as a function of the increment in oxygen content in Fig. 4. This figure shows that high $\Delta CO/\Delta CO_2$ ratios are formed at low oxidation levels and a fast decay up to levelling off occurs as the amount of total oxygen increases.

The above results suggest that similar oxidation levels with similar composition of the surface oxygen groups can be achieved with different types of anode by anodic treatment in NaCl, provided that adequate selection of electrolysis current and time is made. The different performances of the anode materials must be then analyzed in terms of Faradaic oxidation efficiency. The average oxidation efficiency (ε) for the electrochemical oxidation of AC can be derived from the amount of oxygen (O) fixed for a given period of time according to the following equation:

$$\varepsilon = \frac{(O_f - O_i)}{I\,t} \qquad (4)$$

where O_f and O_i stand for the final and initial concentrations of oxygen in the carbon material after and before the electrochemical treatment, respectively; I is the applied current and t is the duration of electrolysis. The average oxidation efficiency (ε) can be alternatively expressed as percentage of used current after multiplying eq. 4 by the mass of treated carbon (m_c) and the theoretical charge consumed per mole of atomic oxygen, 2F (F being the Faraday constant):

$$\varepsilon\,\% = 2\,F\,m_c\,\frac{(O_f - O_i)}{I\,t} \qquad (5)$$

Efficiency percentage (ε%) values are also collected in Table 1. The average oxidation efficiency yields values from nearly 50 % for RuO_2 at low input charges to ca. 10 % for Co_3O_4 anodes.. Overall, efficiency data show that Ti/RuO_2 is the most efficient anode material for the generation of SOGs. This behaviour is most likely to be due to the well-known higher electrochemical oxidation efficiency of Ti/RuO_2-based anodes for the electrogeneration of active chlorine species in chloride-containing electrolytes. One should note that RuO_2-based anodes are currently used in electrolyzers in the chlorine-alkali industry [46]. Barton et al. [27] reported an intermediate efficiency of 28 % with platinised Pt anodes in 0.5 M K_2SO_4 at currents about ten times as low as those used in this work. Therefore, it appears that the electrochemical oxidation of AC performed under the conditions used in this work is comparatively more efficient than that carried out in ref. 27.

In the case of Ti/RuO_2 and Ti/Pt electrodes, the average oxidation efficiency decreases with the applied current, whereas for Ti/SnO_2-Sb-Pt and Ti/Co_3O_4 electrodes the efficiency does not follow a clear trend with the increasing current. In all electrodes, the lowest efficiencies are nevertheless obtained at the highest current tested (1.0 A). These results can be explained considering that the efficiency of side reactions, like oxygen evolution reaction (OER), increases as the current increases.

Quantification of oxygen groups and values of the oxidation efficiency (Table 1) show that the amount of oxygen fixed after 5 h at 0.2 A (4570 μmol/g) is similar to that achieved with the same electrode after 3 h at 0.5 A (4610 μmol/g), but at higher efficiency. From a practical point of view, these results point out that in order to achieve a given oxidation degree, it is more efficient to carry out anodic oxidation experiments at low currents and longer electrolysis times than to employ higher currents for shorter periods of time.

From data in Table 1, it appears clear that the anodic treatment in NaCl produces a higher increase in the CO-evolving groups than in the CO_2-evolving groups, as evidenced by the achievement of CO/CO_2 ratios well above that of the untreated AC sample. Furthermore, data in Fig. 4 clearly point out that CO-evolving groups form predominantly at low oxidation levels, i.e at low passed charges, whereas a higher proportion of CO_2-evolving groups develop at higher oxidation degrees (higher passed charges).

3.2 Comparison between chemical and electrochemical oxidation of AC.

For comparison purposes, conventional chemical oxidation treatments of the same AC material were carried out. Figure 5 shows the CO_2 and CO TPD profiles obtained for the original GAC (W) and those of the GAC samples chemically-treated with different oxidizing chemicals. Table 2 summarizes the quantification of the evolved CO_2 and CO groups, the oxygen content (O) and the CO/CO_2 ratio.

TPD profiles (Figure 5) indicate that, under the present experimental conditions, chemical treatments with HNO_3 and $(NH_4)_2S_2O_8$ lead to an increase in the amount of both types of SOGs (CO and CO_2-evolving groups), in the oxygen content (O) and, consequently, cause the oxidation of the original GAC. On the contrary, the chemical treatment with H_2O_2 slightly increases the amount of CO-evolving groups and the CO_2-evolving groups remain almost unchanged.

According to other authors [12,14,15,19], the use of H_2O_2 as an oxidizing agent of carbon materials produces a low oxidation degree, which seems to be independent of the peroxide concentration [14,15]. On the contrary, an increase in the oxidant concentration does bring about an increase in the AC oxidation degree when HNO_3 is used in the chemical treatment [17].

When results of 2 h-treatments are considered, Figure 5 and Table 2 show that the chemical treatment with $(NH_4)_2S_2O_8$ produces the highest increase in the amount of SOGs of all three chemical treatments. Moreover, the oxidation degree produced by $(NH_4)_2S_2O_8$ increases with the time of treatment, reaching high values after 24 h [18,19].

The plot of the amount of generated CO- and CO_2-evolving groups versus the oxidation level (Fig. 3b) indicates that the overall stoichiometry of the SOGs is rather different for all three chemical treatments and also distinct from the composition of the surface oxides obtained by electrochemical treatment, because CO- and CO_2-desorbing groups develop at rather different rates with the increasing oxidation degree. As to the evolution of the $\Delta CO/\Delta CO_2$ ratio, Fig 4 also shows marked differences in the behaviour of the three chemical oxidation methods treated in this work. The chemical oxidation by HNO_3 yields surface oxygen functionalities with an increasing predominance of groups that desorb as CO. Instead, a chemical treatment with H_2O_2 or $(NH_4)_2S_2O_8$ shows a decrease in the $\Delta CO/\Delta CO_2$ ratio as the oxidation degree rises. The high initial $\Delta CO/\Delta CO_2$ values for H_2O_2 at mild conditions can be explained by the fact that CO_2-evolving groups are almost unaffected by the treatment, i.e. CO-type groups are mainly formed, in agreement with results reported by earlier authors [15]. If the peroxide concentration is raised, i.e. the oxidation conditions become stronger; the oxidation degree rises slightly but the $\Delta CO/\Delta CO_2$ ratio drops abruptly as a consequence of the formation of larger amounts of CO_2-evolving groups. Persulfate treatments show a tendency in the $\Delta CO/\Delta CO_2$ ratio that parallels that obtained for electrochemical oxidation, although with slightly lower values.

In the light of the observed changes in $\Delta CO/\Delta CO_2$ ratios, and considering the low content of SOGs in the original AC (see section 3.1.), it could be proposed that the oxidation of the studied carbon material by both anodic treatment and chemical oxidation with persulfate proceeds via formation of CO-evolving groups being fixed on free surface sites, in agreement with the increase in the $\Delta CO/\Delta CO_2$ ratio observed after any oxidation treatment, whereas CO_2-evolving groups would be formed by oxidation of the existent or fresh CO-evolving groups, thus, justifying the decrease and eventual stabilization of the $\Delta CO/\Delta CO_2$ ratio at longer times of treatment or when the experimental conditions become stronger.

In general, from the comparison between results obtained with both electrochemical and chemical oxidation methods (Tables 1 and 2), it can be stated that for similar times of treatment (2-3 h) the anodic treatment in NaCl can produce oxidation degrees much higher than the chemical treatment with $(NH_4)_2S_2O_8$, which has been found to be the most oxidative chemical method studied in this work. Thus, after a 3 h-treatment, the most efficient anodes (RuO_2 and

SnO_2-Sb-Pt) produce at 0.5 A an oxidation degree similar to that obtained with $(NH_4)_2S_2O_8$ after 5 h; and the oxidation degree achieved with RuO_2 at 1.0 A is even higher than that of $(NH_4)_2S_2O_8$ after 24 h. In addition, results in Figs. 3 and 4 suggest that the composition of the surface oxides formed by chemical oxidation with persulfate is the most similar one to that obtained after anodic oxidation.

According to the few reported studies on comparison between both methods [27], the electrochemical method in 0.5 M K_2SO_4 needed ca. 125 or 180 h, at 50 o 30 mA, respectively to achieve a similar oxidation degree than that produced with 6 M HNO_3, 2 h at 25 ºC,. The markedly low performance of the electrochemical method in that work can be easily explained considering the remarkably different experimental conditions employed by these authors, i.e., a predominant direct electrochemical oxidation in an inert electrolyte at low applied currents, which would give rise to much lower oxidation degrees.

3.3. Influence of time on the anodic oxidation of AC in NaCl and by $(NH_4)_2S_2O_8$

The influence of time of treatment on the surface chemistry of anodically-treated GAC samples was studied with the most oxidizing electrode, a Ti/RuO_2 anode, at 0.2 A (Table 1). As it can be seen, the rise in time of treatment progressively increases the amount of CO_2 and CO-type SOGs. The SOGs generation rate can be followed as the increase in the amount of SOGs (CO, CO_2 and O) with time of treatment. Such an increase in the number of SOGs can be calculated by subtraction of the amount of SOGs at a given time (G_t) minus the initial amount of SOGs (G_0).

Figure 6 depicts a comparison of the time-dependent amount of SOGs generated by electrochemical oxidation at RuO_2 anodes and by chemical treatment with $(NH_4)_2S_2O_8$, since these are the most oxidizing conditions for each method. The generation rate of any kind of

SOG_i is related to the slope of the $(G_t–G_0)_i$ vs. time graph. For calculations, the amount of SOGs was normalized by the specific surface area (S_{BET}) of the used original AC. Results show that the generation rate of the different SOGs with $(NH_4)_2S_2O_8$ is faster at initial or shorter times (at least within the first 2 h) and then, it decreases until the amount of surface groups levels off. On the contrary, the increase in SOGs with time by the anodic treatment at 0.2 A, that is, the oxidation rate, is approximately constant with time, at least during the first 5 h of treatment. The observed tendencies in this preliminary kinetic study suggest that, unlike the chemical treatment, the anodic oxidation process in NaCl is amenable to a much more precise control owing to the observed linear dependence of the oxidation level and amount of SOGs with time. These results are attributed to the fact that, in the electrochemical treatment, the oxidizing species are supplied to the reaction medium at a constant rate determined by the applied current, most probably in the proximity of AC particles, whereas during the chemical oxidation with persulfate, the oxidizing species are in large excess from the beginning and remain nearly constant throughout the treatment.

The advantages of successfully controlling the oxidation degree by the electrochemical method were also underlined by Barton et al. [28]. However, these authors did not use an “active” electrolyte like NaCl and came to the conclusion that the electrochemical treatment spends much longer times than the chemical one to achieve similar oxidation degrees.

In spite of being a process initially (within the first 2-3 h) slower than the chemical treatment with $(NH_4)_2S_2O_8$, the anodic oxidation brings about higher $\Delta CO/\Delta CO_2$ ratios (see Fig 4). According to the proposed oxidation mechanism, the higher values in $\Delta CO/\Delta CO_2$ ratios suggest that the anodic oxidation produces comparatively a higher proportion of CO-evolving groups. On the contrary, the lower $\Delta CO/\Delta CO_2$ ratios observed for the chemical oxidation (Fig. 4) reveal the generation of a higher relative proportion of CO_2-evolving groups than in the case of anodic treatment, what points to a favoured oxidation attack near surface sites with bound oxygen and, therefore, a more aggressive and less controlled oxidation than that obtained during the electrochemical oxidation.

3.4. Effect on textural properties of AC.

Tables 3 and 4 summarize the main textural properties, such as the specific surface area (S_{BET}), the total volume of micropores ($V_{DR}(N_2)$) and the narrowest micropores ($V_{DR}(CO_2)$), for the anodically- and chemically-treated AC samples under different experimental conditions and the untreated (original) activated carbon sample (W).

As it can be observed, and in agreement with previous results [30], the textural characterization shows that the anodic treatment in NaCl produce little modification of the porous texture of the activated carbon in the tested conditions (Table 4). The slight decrease in the textural parameters could be attributed to the increase in the SOGs concentration, which could hinder or block the adsorption of the employed gases during characterization. As it has been previously found [15,20], this slight change in textural properties is also observed after the chemical treatments (Table 4), what seems to indicate that both oxidation processes mainly affect the surface chemistry of the used GAC.

4. Conclusions

Results have shown that the anodic treatment in NaCl with all the tested anodes causes a remarkable oxidation of the AC that progressively increases with the current and time of treatment. The similar shape of the TPD profiles of the electrochemically oxidized AC samples and the linear dependence of the amount of generated CO- and CO_2-evolving groups with the increasing oxidation level suggests that the nature and composition of the anodically formed SOGs is not dependant on the anode nature, but it seems to be characteristic of electrolyses in NaCl medium. This result is consistent with an indirect homogeneous oxidation process, involving highly oxidizing chlorine species electrogenerated in the chloride-containing electrolyte. Moreover, a given oxidation level and composition of the oxygen groups can be achieved with any of the anodes studied, but at a very different Faradaic efficiency. Generally speaking, the faradic efficiency decreases as Ti/RuO_2>Ti/SnO_2-Sb-Pt>Ti/Pt>Ti/Co_3O_4 in good correlation with the ability of each of these electrodes to generate bulk chlorine species.

Provided a proper input current is selected, the anodic treatment in NaCl can produce, during similar treatment times, much higher oxidation degrees in the AC than the conventional chemical treatments with HNO_3, H_2O_2 or $(NH_4)_2S_2O_8$, this latter reagent being the most oxidative substance studied in this work. Neither the chemical nor the electrochemical treatments studied bring about a significant modification of the original porous texture of the studied AC.

The observed change in the $\Delta CO/\Delta CO_2$ ratio with the increasing oxidation level that applies to both the anodic treatment and the oxidation by persulfate supports an oxidation path in which CO-evolving groups are fixed on free sites, and CO_2-evolving groups arise from oxidation of pre-existent or freshly formed CO-evolving groups. The lower values of the $\Delta CO/\Delta CO_2$ ratio for the chemical treatment with persulfate indicate that the oxidation of surface-oxidized sites is favoured in comparison to the anodic treatment, which seems to promote the oxidation of free surface sites instead. Another difference that should be highlighted is that the SOG generation rate in the anodically oxidized AC is constant in the timespan explored, whereas it is initially faster for the AC treated with persulfate and slows down progressively with increasing time until stabilization of the amount of surface groups.

The results reported in this work give credit to the electrochemical treatment in NaCl electrolyte as an efficient and easily controllable technology for the modification of the surface chemistry of activated carbons.

Acknowledgements

Financial support by the Ministerio de Ciencia e Innovación (MAT2010-15273 and CTQ2009-10813) and Generalitat Valenciana and FEDER (PROMETEO/2009/047) projects are gratefully acknowledged.

References

[1] Puri BR. Surface complexes on carbons. In: Walker Jr PL, editor. Chemistry and physics of carbon, vol 6, New York; Marcel Dekker; 1970, p. 191-282.

[2] Bandosz TJ, Ania CO. Surface chemistry of activated carbons and its characterization. In: Bandosz TJ, editor. Activated Carbon Surfaces in Environmental Remediation, Elsevier; 2006, p. 159-230.

[3] Boehm HP. Surface oxides on carbon and their analysis: a critical assessment. Carbon 2002;40(2):145-149.

[4] Burg P, Cagniant D. Characterization of Carbon Surface Chemistry. In: Radovic LR, editor. Chemistry and physics of carbon, vol 30, Taylor & Francis (CRC Press); 2008, p. 129-175.

[5] Leon y Leon CA, Radovic LR. Interfacial chemistry and electrochemistry of carbon surfaces. In: Thrower PA, editor. Chemistry and physics of carbon, vol 24, New York; Marcel Dekker; 1994, p. 213-310.

[6] Rodriguez-Reinoso F. The role of carbon materials in heterogeneous catalysis. Carbon 1998;36:159-175.

[7] Miyake M. Electrochemical Functions. In: Yasuda E, Inagaki M, Kaneko K, Endo M, Oya A, Tanabe Y, editors. Carbon alloys. Novel concepts to develop carbon science and technology, Elsevier Science; Amsterdam; 2003, p. 435-445.

[8] Carrasco-Marin F, Mueden A, Stoeckli F. Water adsorption on activated carbons with different degrees of oxidation. J Chem Soc Faraday Trans I 1997;93(12):2211-2215.

[9] Frackowiak E, Béguin F. Carbon materials for the electrochemical storage of energy in capacitors Carbon 2001;39(6):937-950.

[10] Bleda-Martínez MJ, Maciá-Agulló JA, Lozano-Castelló D, Morallón E, Cazorla-Amorós D. Linares-Solano A. Role of surface chemistry on electric double layer capacitance of carbon materials. Carbon 2005;43(13):2677-2684.

[11] Kamat PV. Graphene-Based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Carbon Support. J Phys Chem Lett 2010;1(2):520-527.

[12] Linares-Solano A, Salinas-Martínez de Lecea C, Cazorla-Amorós D. Nature and Structure of Calcium Dispersed on Carbon. Energy Fuels 1990;4(5):467-474.

[13] Román-Martínez MC, Cazorla-Amorós D, Linares-Solano A, Salinas-Martínez de Lecea C. TPD and TPR characterization of carbonaceous supports and Pt/C catalysts. Carbon 1993;31(6):895-902.

[14] Domingo-Garcia M, Garzón FJL, Pérez-Mendoza MJ. On the characterization of chemical surface groups of carbon materials. J Colloid Interf Sci 2002;248(1):116-122.

[15] de Miguel SR, Scelza OA, Román-Martínez MC, Salinas-Martínez de Lecea C, Cazorla-Amorós D, Linares-Solano A. States of Pt in Pt/C catalyst precursors after impregnation, drying and reduction steps. Appl Catal A 1998;170(1):93-103.

[16] Cheng PZ, Teng H. Electrochemical responses from surface oxides present on HNO_3-treated carbons. Carbon 2003;41(11):2057-2063.

[17] García T, Murillo R, Cazorla-Amorós D, Mastral AM, Linares-Solano A. Role of the activated carbon surface chemistry in the adsorption of phenanthrene. Carbon 2004;42(8-9):1683-1689.

[18] Moreno-Castilla C, Carrasco-Marin F, Mueden A. The creation of acid carbon surfaces by treatment with $(NH_4)_2S_2O_8$. Carbon 1997;35(10-11):1619-1626.

[19] Moreno-Castilla C, Fero-García MA, Joly JP, Bautista-Toledo I, Carrasco-Marín F, Rivera-Utrilla J. Activated carbon surface modifications by nitric acid, hydrogen peroxide, and ammonium peroxydisulfate treatments. Langmuir 1995;11(11):4386-4392.

[20] Figueiredo JL, Pereira MFR, Freitas MMA, Orfao JJM. Modification of the surface chemistry of activated carbons. Carbon 1999;37(9):1379-1389.

[21] Álvarez PM, García-Araya JF, Beltrán FJ, Masa FJ, Medina F. Ozonation of activated carbons: Effect on the adsorption of selected phenolic compounds from aqueous solutions. J Colloid Interf Sci 2005;283(2):503-512.

[22] Pérez-Cadenas AF, Maldonado-Hódar FJ, Moreno-Castilla C. On the nature of surface acid sites of chlorinated activated carbons. Carbon 2003;41(3):473-478.

[23] García AB, Martínez-Alonso A, León y León CA, Tascón JMD. Modification of the surface properties of an activated carbon by oxygen plasma treatment. Fuel 1998;77(6):613-624.

[24] Kyotani T. Control of pore structure in carbon. Carbon 2000;38(2):269–86.

[25] Ishifune M, Suzuki R, Mima Y, Uchida K, Yamashita N, Kashimura S. Novel electrochemical surface modification method of carbon fiber and its utilization to the preparation of functional electrode. Electrochim Acta 2005;51(1):14-22.

[26] Shao YY, Yin GP, Zhang J, Gao YZ. Comparative investigation of the resistance to electrochemical oxidation of carbon black and carbon nanotubes in aqueous sulfuric acid solution. Electrochim Acta 2006;51(26):5853-5857.

[27] Barton SS, Evans MJB, Halliop E, MacDonald JAF. Anodic oxidaton of porous carbon. Langmuir 1997;13(5):1332-1336.

[28] Mehta MP, Flora JRV. Effects of electrochemical treatment of granular activated carbon on surface acid groups and the adsorptive capacity for phenol. Water Res 1997;31(9):2171-2176.

[29] García-Otón M, Montilla F, Lillo-Ródenas MA, Morallón E, Vázquez JL. Electrochemical regeneration of activated carbon saturated with toluene. J Appl Electrochem 2005;35(3):319-325.

[30] Berenguer R, Marco-Lozar JP, Quijada C, Cazorla-Amoros D, Morallon E. Effect of electrochemical treatments on the surface chemistry of activation carbon. Carbon 2009;47(4):1018-1027.

[31] Yoon CM, Long D, Jang SM, Qiao W, Ling L, Miyawaki J et al. Electrochemical surface oxidation of carbon nanofibers. Carbon 2011;49(1):96-105.

[32] Bayram E, Ayranci E. A systematic study of the changes in properties of activated carbon cloth upon polarization. Electrochim Acta 2011;56(5):2184-2189.

[33] Bayram E, Ayranci E. Investigation of change in properties of activated carbon cloth upon polarization and of electrosorption of dye basic blue-7. Electrochim Acta 2010;48(6):1718-1730.

[34] Berenguer R, Quijada C, Morallón, E. Electrochemical Characterization of SnO_2 Electrodes Doped with Ru and Pt. Electrochim Acta 2009;54(22):5230-5238.

[35] La Rosa-Toro A, Berenguer R, Quijada C, Montilla F, Morallón E, Vázquez JL. Preparation and Characterization of Copper-Doped Cobalt Oxide Electrodes. J Phys Chem B 2006;110(47):24021-24029.

[36] Montilla F, Morallon E, Vázquez JL. Evaluation of the electrocatalytic activity of antimony-doped tin dioxide anodes toward the oxidation of phenol in aqueous solutions. J Electrochem Soc 2005;152(10):B421-B427.

[37] Lozano-Castelló D, Suárez-García F, Cazorla-Amorós D, Linares-Solano A. Porous texture of carbons. In: Beguin F, Frackowiak E, editors. Carbons for electrochemical energy storage and conversion systems, CRC Press; 2009, p. 115-162.

[38] Cazorla-Amorós D, Alcañiz-Monge J, Linares-Solano A. Characterization of activated carbon fibers by CO_2 adsorption. Langmuir 1996;12(11):2820-2824.

[39] Cazorla-Amorós D, Alcañiz-Monge J, de la Casa-Lillo MA, Linares-Solano A. CO_2 as an adsorptive to characterize carbon molecular sieves and activated carbons. Langmuir 1998;14(16):4589-4596.

[40] Panizza M, Gerisola G. Electrochemical oxidation of 2-naphthol with in situ electrogenerated active chlorine. Electrochim Acta 2003;48(11):1515-1519.

[41] Rajkumar D, Kim JG, Palanivelu K. Indirect Electrochemical Oxidation of Phenol in the Presence of Chloride for Wastewater Treatment. Chem Eng Technol 2005;28(1):98-105.

[42] Bonfatti F, De Battisti A, Ferro S, Lodi G, Osti S. Anodic mineralization of organic substrates in chloride-containing aqueous media. Electrochim Acta 2000;46(2-3):305-314.

[43] Iniesta J, González-García J, Expósito E, Montiel V, Aldaz A. Influence of chloride ion on electrochemical degradation of phenol in alkaline medium using bismuth doped and pure PbO_2 anodes Water Res 2001;35(14):3291-3300.

[44] Comninellis Ch, Nerini A. Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. J Appl Electochem 1995;25(1):23-28.

[45] Gorgulho HF, Mesquita JP, Gonçalves F, Pereira MFR, Figueiredo JL. Characterization of the surface chemistry of carbon materials by potentiometric tritations and temperature-programmed desorption. Carbon 2008; 46(12):1544-1555.

[46] Trasatti S. Progress in the understanding of the mechanism of chlorine evolution at oxide electrodes. Electrochim Acta 1987;32(3):369-382.

FIGURE CAPTIONS

Figure 1. CO and CO_2 evolution from TPD experiments for the original AC (W) and the anodically-treated AC samples in 2 wt% NaCl for 3 h at different applied currents (A) using different anodes: (a) Ti/SnO_2-Sb-Pt, (b) Ti/RuO_2, (c), Ti/Co_3O_4 and (d) Ti/Pt.

Figure 2. CO and CO_2 evolution from TPD experiments for the original AC (W) and the anodically-treated AC samples with a Ti/RuO_2 anode, at 0.2 A, in 2 wt % NaCl for different times.

Figure 3. Variation of the increment in the content CO- and CO_2-evolving groups versus the increased oxidation degree for: (a) anodically-treated AC samples in: 2 wt% NaCl at Ti/RuO_2 (◆), Ti/SnO_2-Sb-Pt (■), Ti/Co_3O_4 (●) and Ti/Pt (▲) anodes; in 0.5 M H_2SO_4 at Ti/SnO2-Sb-Pt (◇) and Ti/Pt (Δ) anodes; (b) chemically-treated AC samples in H_2O_2, HNO_3 and $(NH_4)_2S_2O_8$ solutions.

Figure 4. Simulated and experimental dependence of $\Delta CO/\Delta CO_2$ ratio on the oxidation level for anodically- and chemically-treated AC samples.

Figure 5. CO and CO_2 evolution from TPD experiments for the original activated carbon (W) and the chemically-treated AC samples with (a) HNO_3, (b) H_2O_2 and (c) $(NH_4)_2S_2O_8$ in different conditions.

Figure 6. Time evolution of oxygen and different oxygen groups during chemical (Q-$(NH_4)_2S_2O_8$) and electrochemical (EQ-RuO_2) treatments (2 wt% NaCl I = 0.2 A).

TABLE CAPTIONS

Table 1. CO and CO_2 evolved from TPD experiments, the total amount of oxygen (O) and the CO/CO_2 ratio of the original AC (W) and the anodically-treated AC samples for 3 h in 2 wt% NaCl at different applied currents and with different anodes. ε = electrochemical oxidation efficiency of AC.

Table 2. CO and CO_2 evolved from TPD experiments, the total amount of oxygen (O) and the CO/CO_2 ratio of the original AC (W) and the chemically-treated AC samples with HNO_3, H_2O_2 and $(NH_4)_2S_2O_8$ in different conditions.

Table 3. Textural characterization of the original AC (W) and the anodically-treated AC samples in 2 wt%NaCl under different experimental conditions.

Table 4. Textural characterization of the original AC (W) and the chemically-treated AC samples with HNO_3, H_2O_2 and $(NH_4)_2S_2O_8$ in different conditions.

Table 1

Sample	**CO μmol g^{-1}**	**CO$_2$ μmol g^{-1}**	**O μmol g^{-1}**	**ε μmol g^{-1} C^{-1}**	**ε (%)**	**CO/CO$_2$**
W	418	393	1204	---	---	1.06
WSnO$_2$ a0.2Cl$^-$ (3h)	1320	643	2606	0.65	25.0	2.05
WSnO$_2$ a0.5Cl$^-$ (3h)	2370	1340	5050	0.71	27.4	1.77
WSnO$_2$ a1.0Cl$^-$ (3h)	2800	1570	5940	0.44	16.8	1.78
WRuO$_2$ a0.2Cl$^-$ (1h)	1280	443	2166	1.34	51.6	2.89
WRuO$_2$ a0.2Cl$^-$ (3h)	1700	793	3286	0.96	37.2	2.14
WRuO$_2$ a0.2Cl$^-$ (5h)	2350	1110	4570	0.93	36.0	2.12
WRuO$_2$ a0.5Cl$^-$ (3h)	2270	1170	4610	0.63	24.0	1.94
WRuO$_2$ a1.0Cl$^-$ (3h)	3270	1760	6790	0.52	20.0	1.86
WCo$_3$O$_4$ a0.2Cl$^-$(3h)	979	376	1731	0.24	9.4	2.60
WCo$_3$O$_4$ a0.5Cl$^-$(3h)	1630	800	3230	0.38	14.4	2.04
WCo$_3$O$_4$ a1.0Cl$^-$(3h)	2290	1160	4610	0.32	12.2	1.97
WTi/Pt a0.2Cl$^-$ (3h)	1510	736	2982	0.82	31.8	2.05
WTi/Pt a0.5Cl$^-$ (3h)	1750	851	3452	0.42	16.0	2.06
WTi/Pt a1.0Cl$^-$ (3h)	2620	1360	5340	0.38	14.8	1.93

Table 2

Sample	**CO μmol/g**	**CO$_2$ μmol/g**	**O μmol/g**	**CO/CO$_2$**
W	418	393	1204	1.06
W-N-23%	1070	728	2526	1.47
W-N-35%	1380	805	2990	1.71
W-N-65%	1710	855	3420	2.00
W-H-10%	652	395	1442	1.65
W-H-20%	729	402	1533	1.81
W-H-33%	829	424	1677	1.96
W-S-2h	1870	1130	4130	1.65
W-S-5h	2070	1320	4710	1.57
W-S-24h	2630	1820	6270	1.45

Table 3

Sample	S_{BET} m^2 g^{-1}	$V_{DR}(N_2)$ cm^3 g^{-1}	$V_{DR}(CO_2)$ cm^3 g^{-1}
W	875	0.37	0.29
$WSnO_2$ a0.2Cl^-	848	0.37	0.22
$WSnO_2$ a0.5Cl^-	769	0.34	0.23
$WSnO_2$ a1.0Cl^-	775	0.35	0.30
$WRuO_2$ a0.2Cl^-	864	0.38	0.30
$WRuO_2$ a0.5Cl^-	792	0.35	0.28
$WRuO_2$ a1.0Cl^-	740	0.33	0.27
$WRuO_2$ a0.2Cl^- 1h	831	0.37	0.29
$WRuO_2$ a0.2Cl^- 5h	783	0.34	0.28
WCo_3O_4 a0.2Cl^-	815	0.34	0.30
WCo_3O_4 a0.5Cl^-	822	0.34	0.23
WCo_3O_4 a1.0Cl^-	735	0.32	0.27
WTi/Pt a0.2Cl^-	824	0.36	0.28
WTi/Pt a0.5Cl^-	772	0.34	0.29
WTi/Pt a1.0Cl^-	810	0.35	0.29

Table 4

Sample	S_{BET} m^2 g^{-1}	$V_{DR}(N_2)$ cm^3 g^{-1}	$V_{DR}(CO_2)$ cm^3 g^{-1}
W	875	0.37	0.29
W-N-23%	840	0.38	0.29
W-N-35%	865	0.37	0.28
W-N-65%	835	0.35	0.28
W-H-10%	851	0.36	0.30
W-H-20%	886	0.38	0.31
W-H-33%	879	0.38	0.28
W-S-2h	864	0.36	0.29
W-S-5h	884	0.38	0.29
W-S-24h	870	0.38	0.30

Figure 1

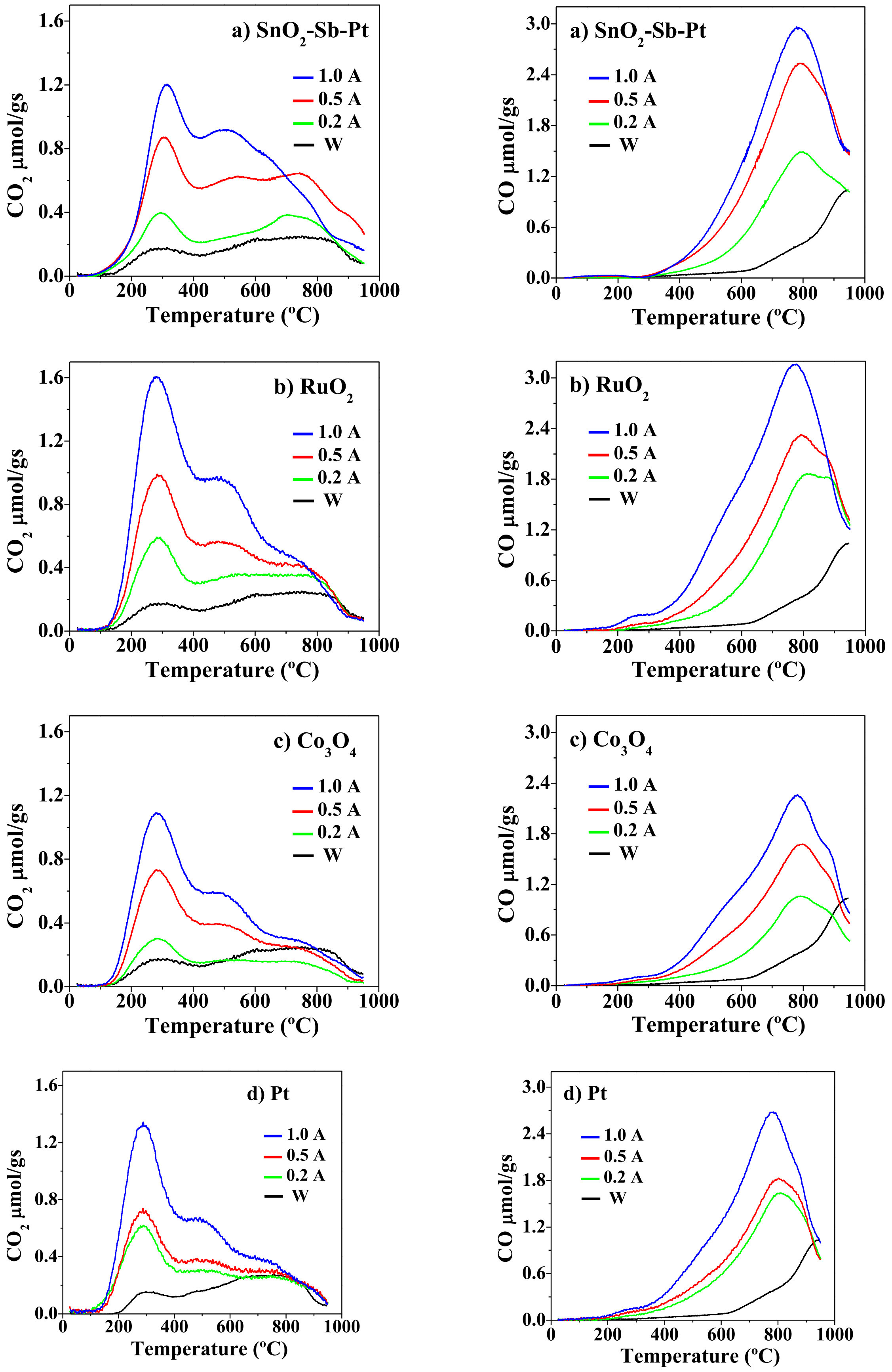

a) SnO$_2$-Sb-Pt
1.0 A
0.5 A
0.2 A
W
CO$_2$ µmol/gs
Temperature (°C)
0.0
0.4
0.8
1.2
1.6
0
200
400
600
800
1000
a) SnO$_2$-Sb-Pt
CO µmol/gs
0.0
0.6
1.2
1.8
2.4
3.0
b) RuO$_2$
b) RuO$_2$
c) Co$_3$O$_4$
c) Co$_3$O$_4$
d) Pt
d) Pt

Figure 2

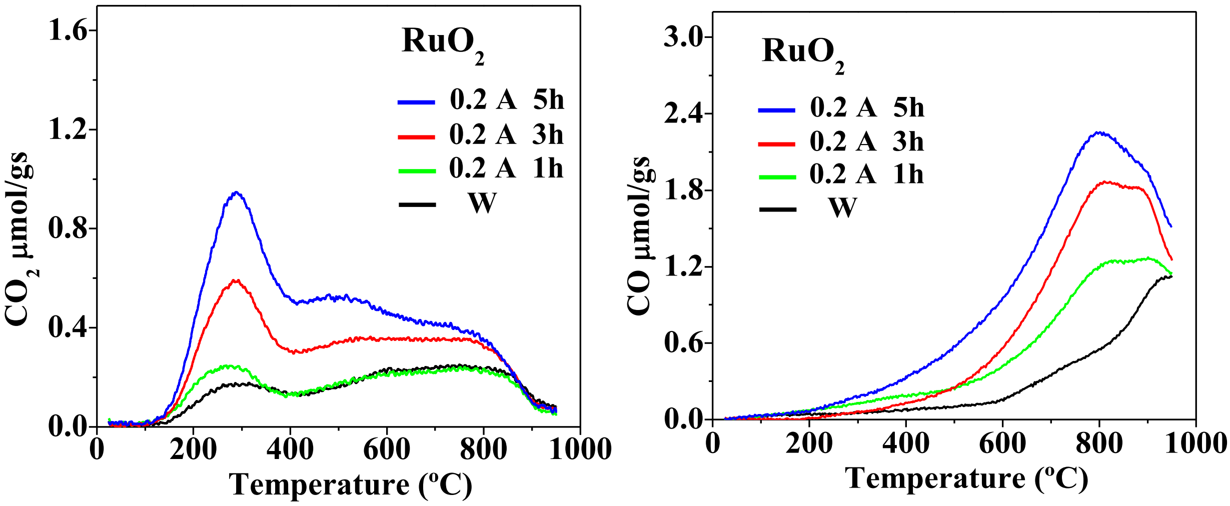

RuO$_2$
0.2 A 5h
0.2 A 3h
0.2 A 1h
W
CO$_2$ µmol/gs
0.0
0.4
0.8
1.2
1.6
0
200
400
600
800
1000
Temperature (°C)
RuO$_2$
0.2 A 5h
0.2 A 3h
0.2 A 1h
W
CO µmol/gs
0.0
0.6
1.2
1.8
2.4
3.0
0
200
400
600
800
1000
Temperature (°C)

Figure 3

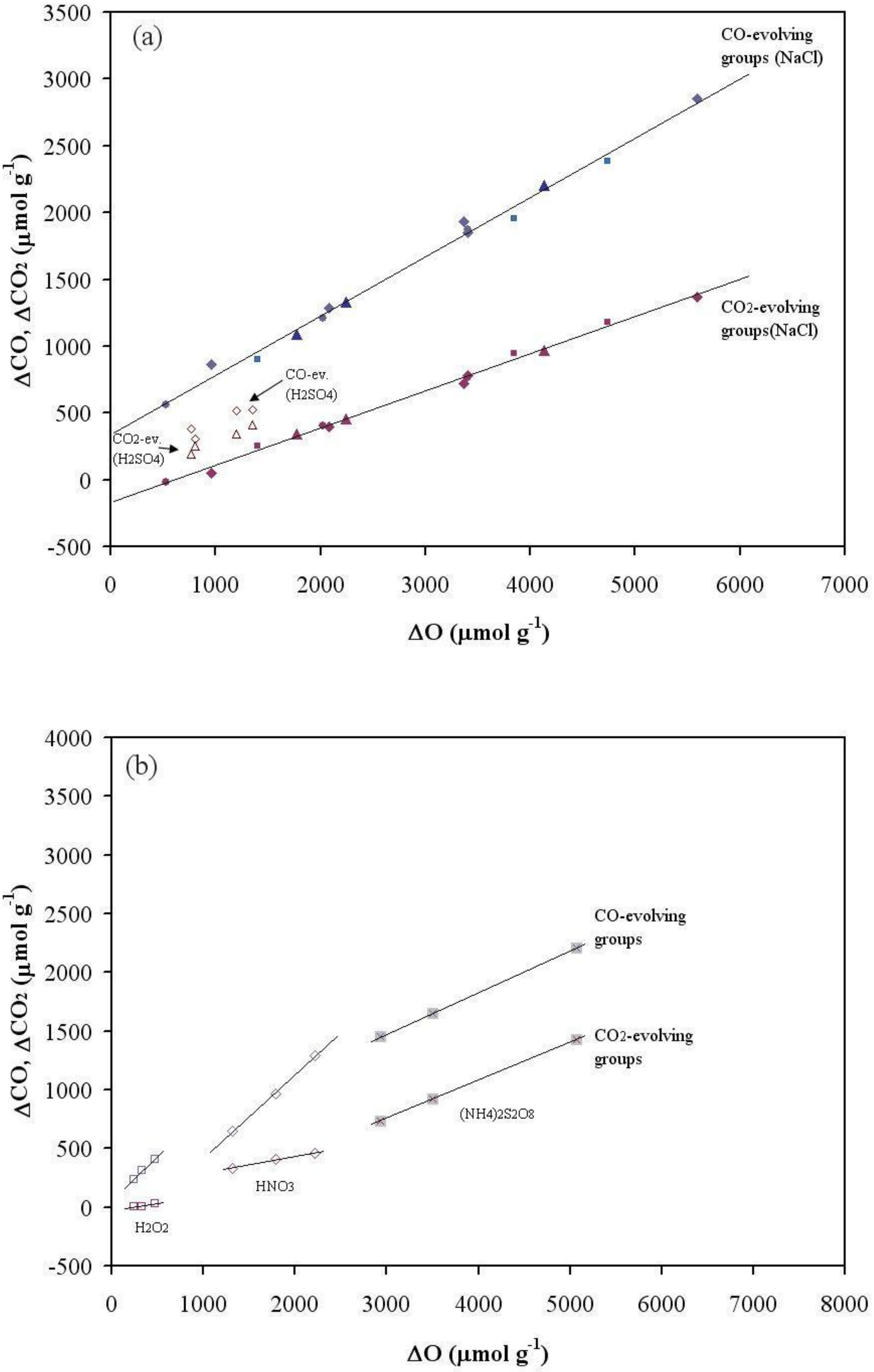

(a)
CO-evolving groups (NaCl)
CO2-evolving groups(NaCl)
CO-ev. (H2SO4)
CO2-ev. (H2SO4)
ΔCO, ΔCO$_2$ (μmol g^{-1})
ΔO (μmol g^{-1})
3500
3000
2500
2000
1500
1000
500
0
-500
0
1000
2000
3000
4000
5000
6000
7000
(b)
CO-evolving groups
CO2-evolving groups
(NH4)2S2O8
HNO3
H2O2
ΔCO, ΔCO$_2$ (μmol g^{-1})
ΔO (μmol g^{-1})
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
1000
2000
3000
4000
5000
6000
7000
8000

Figure 4

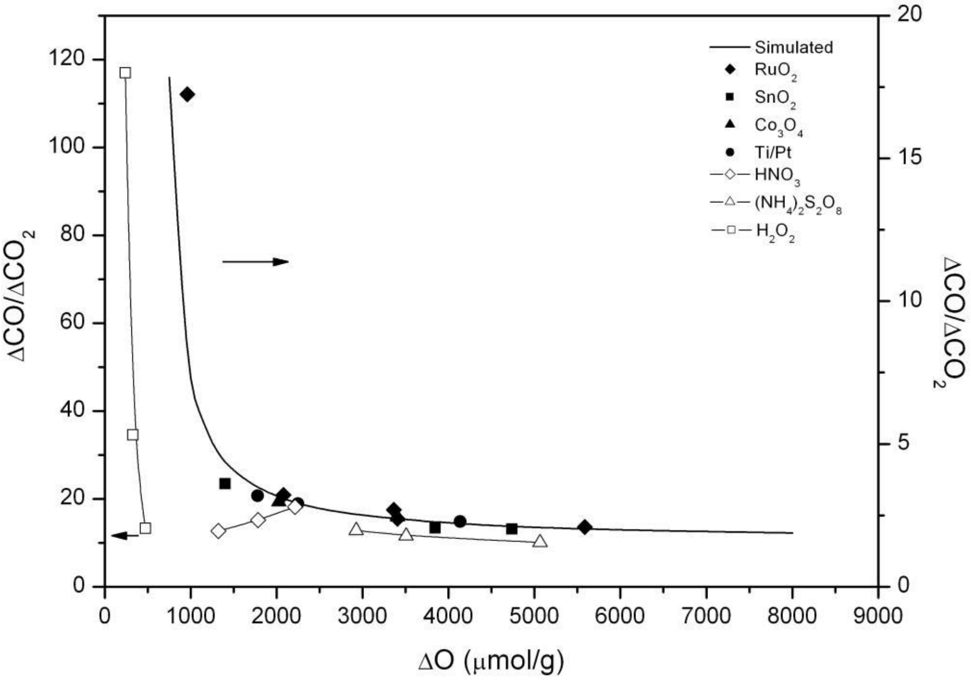

Simulated
RuO$_2$
SnO$_2$
Co$_3$O$_4$
Ti/Pt
HNO$_3$
(NH$_4$)$_2$S$_2$O$_8$
H$_2$O$_2$
ΔCO/ΔCO$_2$
0
20
40
60
80
100
120
ΔCO/ΔCO$_2$
0
5
10
15
20
ΔO (μmol/g)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

Figure 5

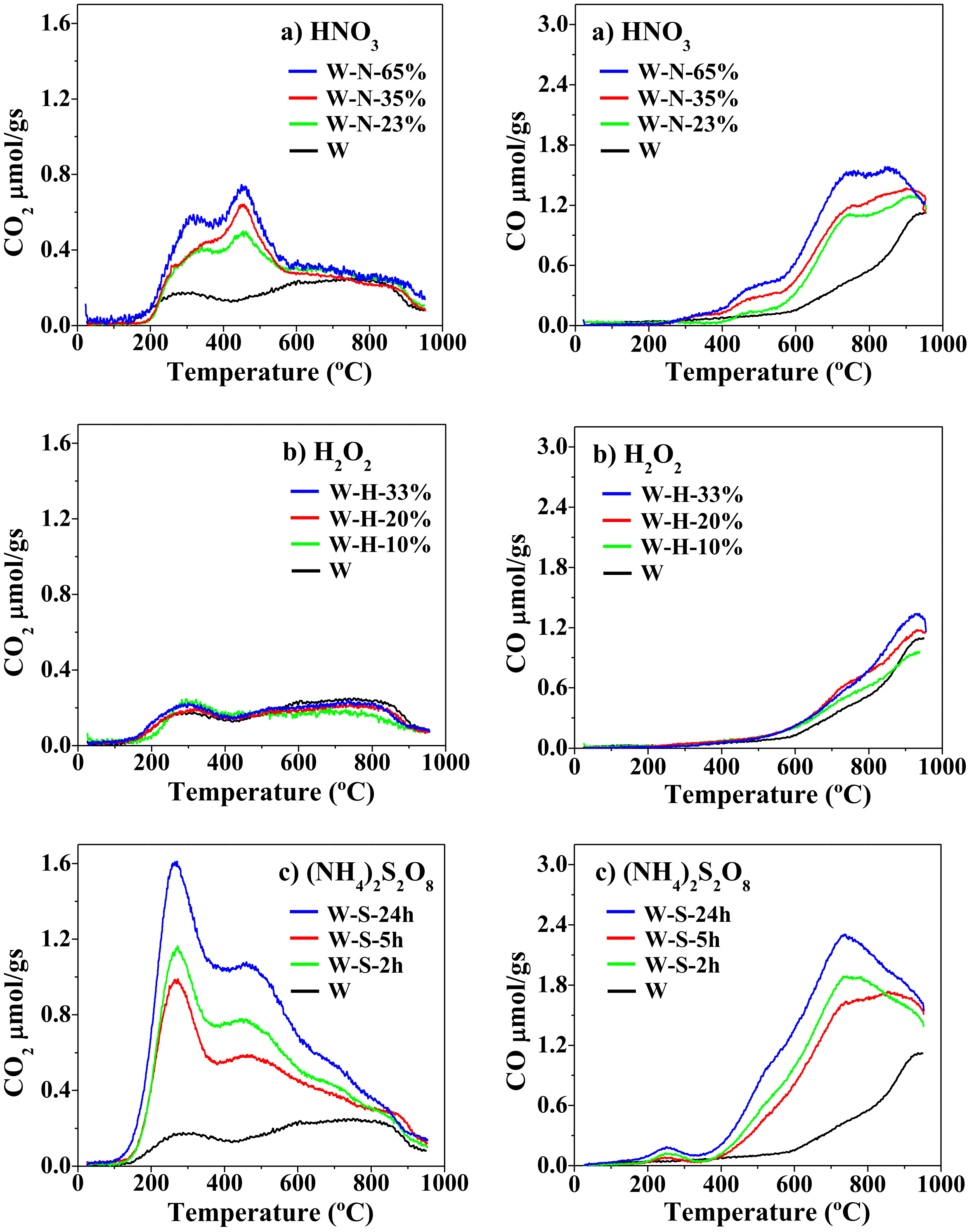
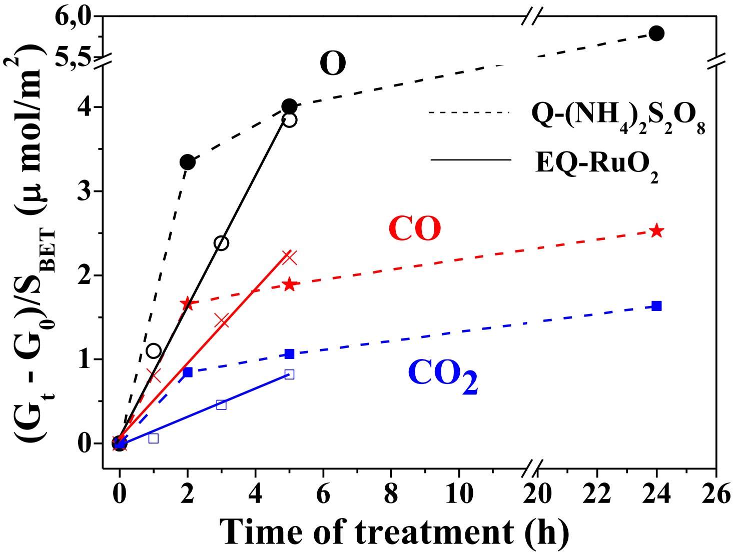

a) HNO_3
W-N-65%
W-N-35%
W-N-23%
W
CO_2 µmol/gs
CO µmol/gs
b) H_2O_2
W-H-33%
W-H-20%
W-H-10%
W
c) $(NH_4)_2S_2O_8$
W-S-24h
W-S-5h
W-S-2h
W
Temperature (°C)
0
200
400
600
800
1000
0.0
0.4
0.8
1.2
1.6
0.6
1.8
2.4
3.0

Figure 6


6,0
5,5
4
3
2
1
0
(G_t - G_0)/S_BET (µ mol/m²)
0
2
4
6
8
10
20
22
24
26
Time of treatment (h)
O
Q-(NH4)2S2O8
EQ-RuO2
CO
CO2