PYROLYZED PHTHALOCYANINES AS SURROGATE CARBON CATALYSTS:
INITIAL INSIGHTS INTO OXYGEN-TRANSFER MECHANISMS

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1. Introduction

Oxygen-transfer reactions of carbon materials are at the heart of fuel combustion and gasification processes. While much progress has been made in achieving their fundamental understanding, the key details of metal/carbon interactions are not fully understood yet, especially regarding mechanisms of the electrochemical oxygen reduction reaction (ORR) [1]. On the other hand, heat-treated phthalocyanines (Pc) [2] have been of interest since the pioneering, but largely ignored, studies of Souma [3-5]. Their intriguing properties have attracted much attention after the discovery that Co-Pc might replace platinum as an electrocatalyst in the ORR [6, 7]; in extensive follow-up studies [8-20] it was reported that a pyrolyzed transition-metal Pc can be even more effective. In addition, more recently pyrolyzed phthalocyanines have been used as raw materials in the production of carbon nanotubes [21-30].

Before fundamental knowledge and practical optimization of the electrocatalytic activity of heat-treated phthalocyanines (and related porphyrin structures) can be achieved, we must understand their catalytic activity in the absence of an electric field. Two main issues are of interest here: (i) the nature of carbon/metal contact, particularly as it influences the transfer of oxygen across this interface; (ii) the degree of metal dispersion on the carbon support surface. In pursuing this goal, these carbonaceous materials must be characterized in terms of their degree of ‘graphitization’ as well as metal-carbon bond survival. The former information is crucial for evaluating the degree of resonance stabilization of the delocalized π -electrons; in an early study, for example, Appleby et al. [31] argued that electrocatalytic activity in ORR is related to “a peculiar ligand field structure which involves a multi-spin state configuration for the central ion”. The latter is needed to assess the extent of catalyst

dispersion on the residual (or skeleton) carbonaceous support: if the phthalocyanine structure is not disrupted, the dispersion of the catalytically active sites (if indeed these reside on the metal atoms) is 100%. Tourillon and coworkers [8] argued that “CoN₄ centers ... are no longer detected after heat treatment in the region of increased activity” and that “the smallest cobalt clusters (20 Å) were observed in the region of highest activity”.

More recently, in a study of a pyrolyzed mixture of Fe phthalocyanine and phenolic resin [16], a direct relation has been found between electrocatalytic activity and nitrogen content. However, that work does not conclude that Fe acts a catalytic center during ORR but it states that “the presence of Fe during carbonization affects the morphology, the degree of edge exposure and nitrogen content in the resulting carbon materials”.

Oxygen-transfer catalysis on carbon surfaces (in the absence of an electric field) is a relatively mature topic, and a reasonably understandable one when discussed in terms of a redox mechanism [32-34]. However, when knowledge of the essential details of electron transfer [35, 36] is required (or is at least desirable), current understanding of the surface chemistry of graphene is not sufficient. In particular, the synergistic effects of iron and nitrogen on the carbon surface – reported almost a century ago [37] – are still waiting for a satisfactory explanation (as well as for some practical applications!).

We report here the results of an ongoing study designed to improve our fundamental understanding of carbons as catalytic materials by focusing on the effects that heat treatment has on the (re)activity of phthalocyanines in two prototypical oxygen-transfer reactions of carbon materials: NO reduction and gasification with O₂. We prepared ‘surrogate’ carbon catalysts by heat treatment (HT) of hydrogen- and metal (M)-containing

phthalocyanines (H-Pc, Co-Pc, Cu-Pc), and thus our goal is to obtain insights about the special role that the **ternary system metal-carbon-nitrogen** is expected to have in the oxygen transfer mechanism of these catalytic reactions. The catalytic activity results, as well as those of selected characterization studies – using elemental and surface area analysis, XRD, Raman spectroscopy, XAFS and XPS – are presented and discussed.

2. Experimental

The raw materials used were H-Pc (29H,31H-phthalocyanine), Co-Pc (Cobalt(II) phthalocyanine, beta form 97%) and Cu-Pc (Copper(II) phthalocyanine) obtained from Sigma Aldrich. To study their relevant structural changes, a heat treatment (pyrolysis) was carried out in a horizontal tube furnace under N₂ flow with a ramp of 5 °C/min and 1-h soak at the final heat-treatment temperature (HTT) of 550, 700, 850 or 1000 °C.

Elemental analyses were performed in a LECO CHN-2000 analyzer as well as a Hitachi Z-8100 atomic absorption apparatus. A volumetric apparatus (Micromeritics Gemini) was used for adsorption characterization (with prior degassing of samples carried out for 24 h at 150 °C and 300 mTorr). For N₂ at 77 K the surface area was obtained with the BET equation, whereas for CO₂ at 273 K it was calculated from the micropore volume obtained by the Dubinin-Radushkevich method and the average micropore slit width determined with the equation proposed by Stoeckli [38, 39]. The XRD analyses were performed with a Rigaku apparatus (Geigerflex D max C; CuK α radiation, λ =0.15418 nm). Raman spectra were obtained using a JASCO NRS-3100 spectrometer with an excitation laser wavelength of 532 nm and power adjusted at 2.4-2.7 mW.

The photoelectron spectrometer used was a JEOL JPS-9010 MX operated at ca. 10⁻⁷ Pa with Mg radiation at 10 kV and 10 mA. Charge correction was carried out by considering that the aromatic C1s peak occurs at 284.5 eV in all samples. The peaks were decomposed (not to be confused with a ‘deconvolution’ procedure [40]) using a Voigt function with both shape factor and width fixed for all peaks of each element. An argon ion beam was used for etching the surface of selected samples during 15 s.

The XAFS measurements on the Co K-edge (High Energy Accelerator Research Organization, Japan, BL-9A beam line, transmission mode) were carried out using samples pelleted with boron nitride; program code FEFF8 was used to calculate the theoretical phase and amplitude for curve fitting.

Oxygen reactivity analyses were performed in a Netzsch thermogravimetric analyzer (STA 409 PC Luxx) using pure air at 100 mL/min and a ramp of 5 °C/min. This is illustrated in **Figure 1**. Between the two most common characteristic temperatures for quantifying reactivity, the onset of ignition and half-life (or temperature at which 50% burnoff is achieved), the latter was chosen; the former was found in this case to suffer from the disadvantage of confusing gasification with decomposition (Figures 1a and 1b). The NO reduction experiments (Figure 1c) consisted of a ramp from ambient temperature to 950 °C at 5 °C/min in a differential quartz reactor loaded with 100 mg of sample under a flow of 500 mL/min NO (1000 ppm, He balance). The outlet NO concentration was monitored with a chemiluminescence analyzer (Horiba CLA-220), while the CO and CO₂ concentrations were measured with nondispersive infrared analyzers (Horiba PIR-2000).

Ancillary computational quantum chemistry experiments were also carried out. Density functional theory (DFT) at the B3LYP level – widely acknowledged to represent a judicious compromise between physical reality and computational expediency and as implemented in the commercially available Gaussian 03 software [41] – was used for the ground state optimization of molecular structures. The basis set was LanL2DZ, commonly used for calculations involving molecules containing transition metals [42].

3. Results

3.1. Elemental analysis

Experimentally determined chemical compositions of as-received H-Pc, Co-Pc, and Cu-Pc (Figure 2) are in good agreement with those calculated from their chemical formulae (shown with an X in the ‘Non-HTT’ part of the abscissa): for example, 10.31 and 10.38% Co in Co-Pc and 10.59 and 11.03% Cu in Cu-Pc, respectively. For all samples, carbon and metal contents increased and nitrogen and hydrogen contents decreased with increasing HTT. The sharp changes between 550 and 700 °C observed for Co-Pc are to be contrasted with the more gradual changes for H-Pc and Cu-Pc. Oxygen was detected (by difference) for samples H-Pc-550, H-Pc-700, Co-Pc-700, and Cu-Pc-700; this is thought to be a consequence of room-temperature air exposure of these carbons, which presumably developed a relatively high and/or active surface area (see Section 4.2), and thus high O₂ adsorption capacity [43, 44], upon heat treatment at intermediate temperatures.

The results obtained here compare favorably with those available in a series of early papers by Souma [3-5]. Quantitative results are very similar, especially in the case of non-HT and samples treated at 1000 °C. Some discrepancies are found for H- and Co-Pc samples treated at intermediate HTT; for example, 5.3 % N in Co-Pc-700 is very different from Souma’s value (20.0%). This issue will be analyzed in Section 3.3, in conjunction with XRD, Raman and computational chemistry results. The temperature ranges of N loss are also in agreement with those reported [16, 45] for HT carbon-supported Pc, indicating that the influence of the substrate on structural stability is not as large as that of the central atom.

3.2. Porosity

Figure 3a illustrates the significant and non-monotonic changes that occur upon heat treatment of Co-Pc: at the higher HTT the uptake of N₂ is higher, whereas it is lower after Co-Pc decomposition at 550 °C. In contrast, the isotherms of H-Pc and Cu-Pc samples (not shown) retain the same shape at all HTTs, but the uptake trends with HTT are again non-monotonic. This is summarized in **Figures 3b and 3c**: (i) in the absence of heat treatment the uptakes, and thus both the apparent and the micropore surface areas, are very low in all cases; (ii) there is a larger amount of nitrogen adsorbed in mesopores of both, as-received Co-Pc and, especially in Co-Pc heat-treated at 700 °C and above; this advantage disappears upon heating at 550 °C (Figure 3b); (iii) In contrast to the BET surface area, where only Co-Pc shows a high sensitivity to HTT (Figure 2b), the DR surface area is much more sensitive to HTT for all samples (Figure 3c). Indeed, the micropore surface area increases by a factor of 17, 20 and 6 for H-, Co- and Cu-Pc samples, respectively. (iv) While all the samples exhibit a maximum surface area at an intermediate temperature, the maximum occurs earlier (at ca. 550 °C) in the absence of a metal (Figure 3c).

A more correct interpretation of the micropore surface area than that afforded by the standard BET method, which still uses the N₂ adsorption results at 77 K, is the subtracting pore effect (SPE) method suggested by Kaneko et al. [46]; it is a modification of the α_s plot [47] that removes the enhanced adsorption effects by both micropore filling and quasi-capillary conditions [46]. The surface areas determined by the SPE method are always lower than the BET values, by ~15% in most cases (not shown), but the tendency is the same for all samples. Although the SPE method is more rigorous, and since no qualitative

difference with respect to BET values exists, the latter will be used in our foregoing analysis.

A comparison between BET-N₂ and DR-CO₂ uptakes is known to be a powerful tool in the analysis of porous structure [48] of activated carbons. Its applicability to heat-treated phthalocyanines is summarized in Figure 4b. For H-Pc samples, CO₂ > N₂ (Figure 4b). This could be due either to their very narrow microporosity or greater abundance of constrictions at micropore mouths [48] that is developed after heat treatment at 550 °C and is gradually lost until total collapse at 850 °C; Figure 4a suggests the latter explanation. In the Co-Pc samples, narrow micropores are also formed at 550 °C; but at 700 °C and above, since N₂ > CO₂, wider pores are developed as well [48], even though Figure 4a shows no evidence of an increasing average micropore size. Finally, in Cu-Pc samples, surface areas measured by both methods are generally low (< 40 m²/g) and, since N₂ ≈ CO₂, this indicated a relatively narrow (Figure 4b) and homogeneous, but underdeveloped microporosity [48].

3.3. XRD, Raman spectroscopy and computational chemistry

The XRD patterns vs. HTT (Figure 5) corroborate the fact that drastic structural changes occur at intermediate HTT, albeit to different extents, depending on the presence and nature of the central atom. Evidence of this is the decomposition temperature of the different samples, which is more clearly seen in selected Raman spectra (see Figure 6), through the transition from the complex Pc molecular spectra to a simpler and characteristic bimodal shape of disordered quasi-graphitic carbons [49]: in the case of H-Pc (around 570 °C for Souma's [3] and <550 °C in our case), Co-Pc (770 °C for Souma's [4] and between 550 and 700 °C in our case) and Cu-Pc (between 550 and 700 °C in both [3] cases). These

differences in decomposition temperatures, between our samples and Souma's, can explain the different elemental analysis results (see Section 3.1). They are more thoroughly analyzed in **Figure 7**: the largest bond length difference among all optimized Pc structures (apart from central atom coordination) occurs at C₃-C₄ and N₂-C₃. Considering this and the fact that bond length is inversely proportional to its strength, it is expected that sample stability is in the order Co ≥ Cu >> H; this is indeed consistent with the experimental results.

It is interesting to note that the development of crystalline order in the H-Pc samples is relatively poor and similar to Cu-Pc (see **Table 1**) whereas the quasi-graphitic stack in the Co-Pc is almost four times higher. There is very little evidence of L_a growth (at ca. 42° 2θ) whereas the average crystallite height (L_c around 2 nm for H-Pc and Cu-Pc and above 7 nm for Co-Pc) is in all cases higher than that [50] of carbons derived from coals (L_c= 0.98 nm) and biomass (L_c= 0.88 nm) at the same HTT, but very similar to graphitizing carbons reported by Franklin [51] treated at 1000 °C.

In the absence of a central metal atom, the heterocyclic structure is disrupted at the lowest HTT (550 °C). In contrast, this structure does not break up until 700 °C in Co-Pc and Cu-Pc (note that a peak corresponding to the original Co-Pc structure around 2θ=7° persists at 550 °C); nevertheless, the evidence for the formation of turbostratic carbon at low HTT is clearest for the Co-Pc samples (see also Table 1).

The metallic phases present in these samples are identified as fcc Co⁰ (JCPDS card 15-0806, peaks at 2θ=44.1° and 51.5°) and fcc Cu⁰ (JCPDS card 4-0836, peaks at 2θ=43.2° and 50.4°). The small hump observed for Cu-Pc-700 at 2θ=36.3° (see Figure 5c) corresponds to

the most intense reflection of Cu₂O (JCPDS card 5-667). The origin of the low-angle peak at $2\theta=11^\circ$ corresponding to a periodicity of 0.80 nm (which is absent from Co-Pc and Cu-Pc samples) is intriguing and has not been clarified. At least five possible structures have been reported to produce this phenomenon: (i) a graphite oxide plane (001) reflection, occurring at $2\theta=10.9^\circ$ [52], is discarded because it is independent of the oxygen content of the samples (see Figure 2a) compared to O/C ratio of at least 0.34 for graphite oxide [53]. (ii) A reflection at $2\theta\sim 12^\circ$ was assigned to plexiglas sample holder in a study of HT phthalocyanines supported on carbon black [54]. **However**, this cannot explain why in our case the low-angle reflection appears only in the case of H-Pc. (iii) Templated carbons synthesized from mordenite exhibit long-range-order periodicity around 0.9 nm (equivalent to $2\theta\sim 10^\circ$) corresponding to a row of channels in the (002) plane of the template where carbon is deposited [55]. (iv) The presence of a discotic phase with an average center-to-center distance between columns of partially pyrolyzed raw molecule (PTCDA: 3,4,9,10-perylenetetracarboxylic dianhydride) produces a low-angle peak at $2\theta=9^\circ$ [56]. A similar peak appears at $2\theta=7^\circ$ for mesophase pitch [57], and corresponds to the nominal lateral dimensions of its constituent molecules. (v) In a theoretical x-ray scattering study of polyaromatic carbons [58], a reflection which is not discussed in the article appears at $2\theta\sim 12^\circ$ when two or a few more layers are stacked along the c-axis, which is similar to the previous case. Among all these possible causes, the most likely one is that some parallel long-range stacking occurs upon HT, similar to β -type Pc crystal structure [3], which is concurrent with the growth of (002) quasi-graphitic layers.

3.4. XAFS

Figure 8 shows the Co K edge XANES and the Fourier transform spectra of the Co K edge EXAFS. The local structural parameters are collected in Table 2. The pre-edge structure of the XANES is sensitive to the symmetry around Co atoms; the XANES part of the spectra indicates that, when HTT is increased from 550 to 700 °C, cobalt atoms undergo a structural change, from square-planar to fcc. In an analogous case [59], with phthalocyanines supported on activated carbon, such a change occurred between 700 and 800 °C, suggesting that the carbon has a stabilizing effect on the phthalocyanine structure. The transition labeled as *1 in Figure 8a at 7716 eV is a fingerprint of the Co-N₄ square-planar environment of the raw material [59]: at 700 °C and above it disappears, indicating that such local structure is not stable at higher HTT.

An analysis of the EXAFS part of the spectra (see Figure 8b) also shows that a structural transition occurs above 550 °C when the nearest neighbor of the Co atom changes its distance from 1.92 to 2.50 Å (see Table 2), the first being characteristic of the Co-N bond in Co-Pc [60, 61]. The second is characteristic of Co-Co bond in metallic cobalt, either hcp or fcc; these are the most common cobalt structures under these conditions, undistinguishable by EXAFS alone – Co-Co nearest neighbor distance is 2.50 Å for hcp and 2.52 Å for fcc (JCPDS 05-0727 and 01-1259) – although it is known that the transition from hcp to fcc occurs between 653 and 690 K [62].

Expected coordination numbers of extreme samples are 4 in the case of the square-planar structure of Co-Pc and 12 in the case of Co⁰ (both for fcc and hcp since they are close-packed structures). Experimentally (see Table 2), the coordination number of Co-Pc

decreases slightly from 3.4 to 3.2 upon HT at 550 °C, meaning that there is a smaller number of nitrogen atoms surrounding the cobalt atom. In the case of the metal-like samples ($\text{HTT} \geq 700$ °C) the coordination number consistently increases from 8.5 to 9.9 (Co-Pc-700 and Co-Pc-1000, respectively) indicating an increase in the order (and size) of the metallic cobalt crystals; these should not be large since the reference value for cobalt foil (11.5) is much higher. The Debye-Waller factor (DWF) indicates an attenuation of x-ray scattering by thermal motion and it increases with structural distortion. The reasons for its decrease in Co-Pc-550 compared to Co-Pc are unclear: the latter is pure and not yet thermally decomposed, in contrast with the metal-like samples where DWF decreases monotonically, approaching a value closer to that of cobalt foil.

It is interesting to note that there is some difference in the XANES part of the spectrum between high HTT samples and Co-foil (see label *2 in Figure 8a): the peaks for the transition around 7726 eV are not fully separated for Co-foil compared to Co-Pc-1000, indicating that the Co structures are still somewhat different. This discrepancy does not occur in the study by Martins Alves et al. [59], where the Co^0 spectrum was different from that reported by us and in the literature [63-65] and the peaks are not separated; such an effect could be attributed to different sizes of the metal clusters, as shown in a recent study [65].

3.5. XPS

We compared the spectra of as-received and heat-treated Co-Pc samples, as well as spectra of all three samples heat-treated at 850 °C, and we analyze them in turn below.

3.5.1. Effect of HTT

The dominant contributors to the C1s peak in as-received Pc samples are 24 benzene-like and 8 pyrrole-like aromatic carbons but, since other contributions are present [66, 67], this ratio is apparently not observed (see Figure 9a); its evolution with HTT shows a decrease of pyrrole-like carbon bonding and its characteristic peak (at 285.7 eV) becomes similar to the asymmetric peak found in more homogeneous graphite-like carbons (see Figure 10a).

Evidence for the presence of surface nitrogen (N1s peak, see Figure 9b) is a single peak centered at 399.0 eV, in agreement with the literature [68-70]; there is little separation (e.g., 0.28 eV as a shift in Pb-Pc [71]) between the four equivalent aza-type nitrogens and four equivalent pyrrole-type nitrogens (for both Co- and Cu-Pc). The decrease in surface nitrogen content with HTT is consistent with the disappearance of the C1s peak at 285.7 eV (attributed to carbon-nitrogen bonding, as mentioned above) and is practically undetected at 850 °C and above. The peak corresponding to Co 2p_{3/2} (Figure 9c) in as-received Co-Pc occurs at 781.3 eV and its intensity decreases with HTT without appreciable change in its binding energy (781.2 eV at both 550 and 700 °C) which is 0.7 eV higher than that reported [69] for Co-N in phthalocyanines but is considered to be an acceptable result since metallic and oxidized cobalt should appear below this energy [69, 72]. At 850 °C and above, Co 2p_{3/2} is no longer detectable: this is interpreted as evidence of metal sintering and encapsulation of metal particles by the growing carbon layers [11, 16]. Regarding the O1s peak, its intensity and binding energy (532.5 eV) are practically constant with HTT (see Figure 9d) for all samples.

Ion etching was performed in the sample heat-treated at 850 °C (shown in grey behind its corresponding non-etched Co-Pc-850 spectra in Figure 9). It reveals at least three

interesting changes: (i) the shoulder at ca. 286 eV shows that the carbon is more heterogeneous than in the non-etched surface due to the (ii) increased presence of nitrogen inside the particles; and (iii) the binding energy of Co 2p_{3/2} is lowered to 779.0 eV, which is close to that of metallic cobalt at 778.0 eV [72].

In **Figure 10b** the predominance of lower-energy aza peak in H-Pc samples is shifted towards the pyrrole peak at 850 °C. This is quantified in **Table 3** where the aza/pyrrole ratio changes from 2.0 to 0.6, meaning that the pyrrole state of nitrogen is more stable; the deviation from theoretical value of 3 for H-Pc (six aza-N composed of two central aza-N and four meso-bridging aza-N vs. two pyrrole-N) is due to the presence of a satellite photopeak [73] (not shown here).

In case of metal-containing samples, separation of the broad N1s hump into two peaks after HT (contrast Figure 9b with 10b for the case of Co-Pc) indicates that the metal has less influence than carbon over the atomic environment of nitrogen. Quantitative information summarized in Table 3 includes binding energies for both pyrrole and aza nitrogen and its ratio: the similar increase for both metals (ratio of 1.0 in the theoretical case for as-received samples, 1.3 for Cu-Pc-850 and 1.5 for Co-Pc-850) indicates that a new pyrrole peak, as that found in metal-free Pc bonding nitrogen to hydrogen and two carbons, is present after HT and in similar amount compared to the meso-bridging aza-N and metal-N pyrrole (both of which have a small binding energy difference and are thus not amenable to separate identification).

3.5.2. Effect of coordination atom

The C1s spectra for all samples heat-treated at 850 °C are compared in Figure 10a and include as a reference the spectrum of Madagascar graphite. The main difference among all samples lies in the narrow 285-287 eV region, i.e., carbon singly bonded to more electronegative atoms or increased presence of sp^3 carbon-carbon bonding. Qualitative information about heteroatoms bound to carbon can be obtained by comparison with the sharp C1s peak characteristic of natural graphite, in order of similarity: Madagascar > Co-Pc-850 > Co-Pc-850 etched > H-Pc-850 $\geq$ Cu-Pc-850, where the inverse trend with respect to nitrogen content – i.e., Co-Pc-850 < H-Pc-850 $\leq$ Cu-Pc-85 (see Figure 8b) – confirms that the differences in the extent of C-N bonding are a consequence of having different coordination atoms.

4. Discussion

4.1. Structural changes

The main findings presented in Section 3 are summarized in Figure 11, which highlights parallels among the coordinating atoms as well as differences in the changes occurring with heat treatment. The porosity, especially in the micropore range, is developed only after the original phthalocyanine structure is destroyed; but this process occurs in different temperature ranges, metal-containing samples being the most refractory. The details of pore size evolution also depend on the coordinating atom: they are especially sensitive to it in the case of H-Pc and Co-Pc, both of which exhibit the highest microporosity development

at intermediate temperature in a manner reminiscent of activated carbons [74] and other cokes and chars [75].

The critical index of structural integrity or collapse is the N content, and it too depends on the Pc coordinating atom: it is noteworthy, for example, that its temperature window is much narrower in the case of Co-Pc. The fate of the metal is of course related to that of N, the expectation being that there is a correlation between the loss of N and the detection of metal particles either on the carbon surface or trapped inside the evolving carbon structure. Even though, as shown in Figure 7, there is evidence of metallic Co and Cu above $\text{HTT}=700\text{ }^{\circ}\text{C}$, the results for Co-Pc are the most telling in this regard: while the XPS spectra (Figure 9c) contain no evidence of cobalt on the external surface, the XRD and EXAFS profiles show that Co^0 has been formed. In particular, the XPS ion etching results (see Figure 9c) confirm the presence of metallic cobalt in subsurface regions (approximate etched depths for C, Co and Cu are 1-2 nm, 13 nm and 20 nm, respectively). Whether or not these results may be interpreted as evidence for the long-known synergy between a transition metal and nitrogen on the carbon surface [37] deserves closer scrutiny: note that the etching procedure reveals the presence of nitrogen in the same subsurface regions; but the cobalt peak (Figure 9c) is displaced at $850\text{ }^{\circ}\text{C}$ towards metallic Co and thus Co is unlikely to be coordinated with N, whereas the carbon peak displays a higher-binding-energy shoulder, which might be indicative of a C-N bonding. The implications of these findings for the chemical reactivity behavior of heat-treated phthalocyanines are discussed in Section 4.2.

The differences in N/C atomic ratio between elemental analysis and XPS (see Figure 12) indicate a heterogeneous radial distribution in the particle: at most HTT analyzed, surface

N/C is almost twice that of bulk; an exception is seen in the case of Co-Pc HT above 550 °C where total bulk N/C is very similar to the surface value. Since XPS analysis probes deeper into the particles than the longest distance to a N atom in the Pc molecule, the surface and bulk N/C were expected to be similar at low HTT; this was not the case and its implications require additional analysis.

4.2. Effect of heat treatment on reactivity

The O₂ reactivity of the heat-treated H-Pc samples decreases monotonically with HTT (see **Figure 13**), a trend that is typically observed for most carbonaceous solids [76, 77]. Since their porous structure is very similar (at least as evidenced by their N₂ adsorption isotherms), this can be attributed to two effects: (i) the well documented annealing and loss of (re)active surface area [76, 77]; and (ii) a decrease in the N/C ratio, because the presence of N in the carbon structure presumably increases carbon's reactivity towards oxygen [78, 79]. The O₂ reactivity results for metal phthalocyanines are quite different: the presence of the metal decreased by more than 100 °C both the ignition temperature (Figure 1) and the half-life temperature (Figure 13) with respect to the metal-free samples. For both Cu-Pc and Co-Pc samples there is an optimum HTT, which is more pronounced in the latter case; this is attributed to a more complex interplay among carbon surface annealing, Pc structure and porosity collapse and gasification catalyst dispersion due to metal crystallite growth.

Microporosity development can account for the initial reactivity increase for Co-Pc (see Figure 3c) but not for Cu-Pc (see Figure 3b). In this context the findings of van Veen and coworkers [18] are relevant: in a study of HT carbon-supported metalloporphyrins and phthalocyanines they concluded that the “continued existence of the MeN₄ moiety of the chelate is the structural feature which is associated with the high activity of heat-treated

materials”. Our results are in agreement with this argument: at low HTT, the incipient carbon structure is expected to retain the MeN₄ moiety (see Figures 2b, 2c, 7, 9b and 10b), which in turn is expected to have a very high specific activity compared to carbons with and without metals, according to the measurements of Rideal and Wright [37] **for carbon-metal-nitrogen systems** (C-C : Fe-C : Fe-C-N = 1 : 50 : 800). At the higher HTT, the sintering of metal particles and loss of reactive surface both conspire to reduce the O₂ reactivity, as shown in Figure 13.

The NO-carbon reaction [80] has been of increasing interest, because of its importance in coal combustion and gasification, as well as the potential for using carbons as effective catalysts and/or reducing agents in NO mitigation [81, 82]. From a fundamental standpoint, it is also an oxygen-transfer reaction, but its mechanism is even more complex than that of the O₂-carbon reaction [32, 83]. This is illustrated by the following set of key reactions [34], the latter two being common to both mechanisms.

Figure 14 shows the effect of HTT on the evolution of CO and CO₂ for Co-Pc samples. As illustrated in Figure 1c, it commonly starts at ca. 500 °C and is essentially complete below 700 °C, except for the highest HTT, but the conversion of NO was not monotonically dependent on HTT. Reactivity does not seem to be controlled by surface area differences since there is no correlation with either the BET or the DR surface area. As expected, CO₂ evolution occurs at lower temperatures and is more pronounced for the lower-HTT

samples; this is in agreement with the principle, now confirmed both experimentally [84, 85] and theoretically [86], according to which CO₂ formation is favored by the relative abundance of mobile oxygen surface complexes, predominantly of the epoxy type [87, 88]. Nevertheless, the evolution of CO is seen to be the dominant reaction (compare the scales in Figures 14a and 14b), which is a disadvantage in the development of effective NO reducing agents [89]. These CO profiles are confirmed to be as complex as those reported in our earlier study [90], in which we used inexpensive cobalt-doped active carbons lacking nitrogen. The following differences and similarities are interesting to point out: (i) Co-Pc displays higher catalytic activity than Co-C (cobalt-loaded chars prepared by either ion exchange or incipient wetness impregnation); (ii) Cu-C was more reactive than Co-C in contrast to their Pc-counterparts (see Figure 13); (iii) metal-loaded chars were most reactive at low HTT; (iv) similar oscillatory behavior was observed in NO reduction at high temperatures due to Co-catalyzed carbon gasification by CO₂; and (v) preferential desorption of CO was detected, which indicates low surface oxygen coverage for the NO reduction. The implications of these findings are discussed next.

4.3. Importance of oxygen transfer in catalytic activity

Oxygen transfer on carbon surfaces is a complex phenomenon even in the absence of catalytic metal impurities [91]. In the presence of a metal, the key issue is the interaction of oxygen at the M-C interface. In this context, the role and changes undergone at the original M-N-C bonding in M-Pc samples is of special interest.

While evidence for the special role of **M-N-C** bonding [37] remains elusive, it is interesting to note the strong effect produced by the central atom by comparing catalyzed and uncatalyzed O₂ reactivity (see Figure 13): the metal upon thermal stressing gives more stability to the Pc molecule, but in an oxidizing environment, its main role is that of a gasification catalyst, which more efficiently transfers oxygen towards the most reactive edge atoms in the incipient char structure.

5. Conclusions

The relationships among structural and chemical changes occurring after HT of H-, Co- and Cu-Pc and their reactivity in an oxidizing environment are complex but tractable: the constant loss of reactivity with increasing HTT in the case of H-Pc is attributed simply to annealing and loss of heteroatoms with almost no influence of porosity. The metal-containing phthalocyanines exhibit an optimum in reactivity at intermediate HTT, strongly correlated to its micropore surface area and sintering of metal particles; in this regard is surprising to note that nitrogen content and reactivity are not related. The change in the mechanism of gasification is also very clear from the comparison of Pc samples with and without the coordinating metal: while enhancing thermal stability, the metal also acts as a catalyst, which allows the heat-treated phthalocyanine to participate in oxygen transfer reactions at temperatures that are much lower than those of its decomposition.

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Table 1: Effect of heat treatment on stack height L_c (nm)			
HTT	Metal-free	Cobalt	Copper
Non	-	-	-
550	2.0	2.6	-
700	1.6	2.6	1.3
850	1.7	3.7	1.4
1000	2.0	7.4	1.8

Table 2: Local structural parameters for as-received and heat-treated cobalt phthalocyanines and Co foil: neighboring atom (X), coordination number (N), bond length (R), and Debye-Waller factor (DWF)

	Co-X	N	R (Å)	DWF (Å)
Co-Pc	N	3.4	1.92	0.058
Co-Pc-550	N	3.2	1.91	0.045
Co-Pc-700	Co	8.3	2.50	0.082
Co-Pc-850	Co	9.3	2.50	0.082
Co-Pc-1000	Co	9.9	2.50	0.079
Co foil	Co	11.5	2.49	0.072

Table 3: XPS quantification for N1s peak in selected samples			
	Pyrrole-N energy (eV)	Aza-N energy (eV)	Aza/pyrrole area ratio
H-Pc	400.2	398.6	2.0
H-Pc-850	401.0	398.3	0.6
Cu-Pc-850	400.6	398.4	1.3
Co-Pc-850 etch	400.4	398.6	1.5

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

<u>X=</u>	<u>H-</u>	<u>Co-</u>	<u>Cu-</u>
N ₁ -X:	1.018	1.952	1.984
C ₁ -N ₁ :	1.394	1.397	1.394
C ₁ -C ₂ :	1.459	1.461	1.464
C ₁ -N ₂ :	1.331	1.333	1.338
N ₂ -C ₃ :	1.347	1.333*	1.338*
C ₃ -C ₄ :	1.473	1.461*	1.464*
C ₃ -N ₃ :	1.388	1.397*	1.394*
C ₅ -C ₆ :	1.422	1.421	1.420

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14