

New Insights about the Selectivity in the Activation of Hydrogen Peroxide by Cobalt or Copper Hydrogel Heterogeneous Catalysts in the Generation of Reactive Oxygen Species

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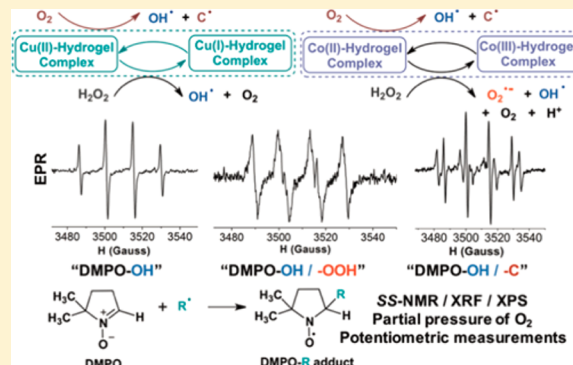
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Supporting Information

ABSTRACT: We report the performance of Co(II) and Cu(II) coordination complexes on H₂O₂ activation. The heterogeneous catalysts containing aliphatic amine, *N*-heterocycle, and/or carboxylic acid ligands in hydrogel materials coordinated with Co(II) or Cu(II) were used in this study. These complexes were characterized by solid-state NMR, X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence techniques in order to quantify the superficial and bulk metal ion centers together with the aim of elucidating the ligands involved in the uptake of Co and Cu ions. The release of free radicals on H₂O₂ activation and the identity of reactive oxygen species were studied by spin trapping using DMPO in electron spin resonance (ESR) experiments. The Co(II) complex/H₂O₂ systems produced O₂, anion superoxide (O₂^{•-}), and hydroxyl radical (OH[•]), which diffused into the solution at the time that a decrease in pH was detected. A possible catalytic mechanism would involve the Co(II)/Co(III) redox couple, according to XPS results. In the same way, the Cu(II) complex/H₂O₂ systems produced O₂ and OH[•], with evidence of Cu(II)/Cu(I) redox cycle. For these catalytic systems, there was no direct evidence of intermediary reactive species. The identity of the ligands played a crucial role in the efficiency of catalytic activation. In addition, in the absence of H₂O₂, the dissolved O₂ was activated by most of the complexes tested, releasing only OH[•].



1. INTRODUCTION

The need for clean technology either for fine chemistry or for waste treatment leads to the replacement of traditional inorganic oxidants such as K₂Cr₂O₇ and KMnO₄ by benign, easy-to-handle oxidants, such as H₂O₂ and O₂.

H₂O₂ is an ideal alternative reagent for oxidation reactions in aqueous solutions because the reduced product is H₂O. The H₂O₂ activation performed by heterogeneous catalysts involves recognized advantages such as phase separation by coarse filtration and recycling. The efficiency can be affected when the active sites are not completely accessible to the substrate and when some of them are present in the form of surface defects.

The activation can be achieved by nonmetal catalysts as well as polyoxometalates or transition-metal ion complexes with

organic ligands. In particular, the so-called Fenton and Fenton-like reactions produce the release of reactive oxygen species (ROS) from H₂O₂ through transition-metal-mediated pathways.^{1–3} The decomposition of H₂O₂ by the catalytic cycle of Fe(III)/Fe(II) produces OH[•] and ferryl ion (Fe(IV)), the last one being the dominant oxidant at neutral pH.⁴ In a similar way, H₂O₂ can produce OH[•] via the Cu(II)/Cu(I) cycle involving different reaction pathways which complicates the thorough elucidation of the mechanism.⁵

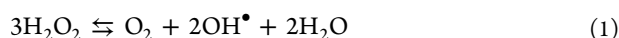
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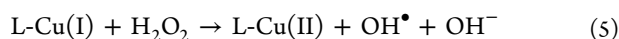
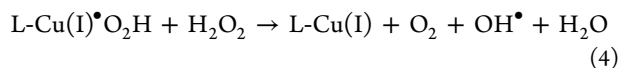
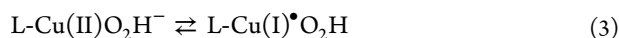
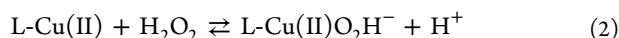
We have explored the heterogeneous catalysis of H₂O₂ activation using Cu(II)-polymer complexes, where the ligand was either a polyampholyte derived from ethylene glycol diglycidyl ether (EGDE), methacrylic acid (MAA) and imidazole (IM) (named *poly*(EGDE-MAA-IM)),⁶ or a polyelectrolyte derived from EGDE and 1,8-diamino-3,6-dioxaoctane (DA) (named *poly*(EGDE-DA)).⁷ The Cu(II)-polymer/H₂O₂ released gas bubbles and OH• free radicals detected by spin trapping experiments with DMPO. The pH value did not vary significantly at the time that the partial pressure of O₂ increased together with the concentration of free radicals.

Based on previous studies on H₂O₂ activation catalyzed by copper complexes,^{6,7} a possible reaction could be considered:



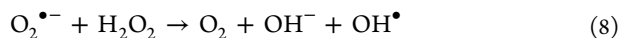
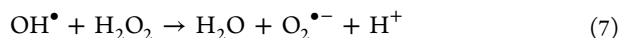
In addition, there are two mechanisms for this stoichiometry: an inner-sphere and an outer-sphere mechanism.

Regarding the inner-sphere mechanism, and according to Pecci et al., the steps could be⁸

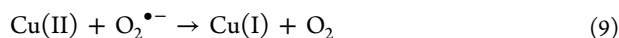


H₂O₂ would bind in a coordination site of Cu(II) in the place of a H₂O molecule or other weaker ligand. The radical OH• would react with the excess of H₂O₂ or dimerize. The authors mentioned that the O₂ production by H₂O₂ in the homogeneous system with Cu(II) was detected only at high concentration of H₂O₂.

In the inner-sphere model, Perez-Benito presented three different reaction pathways according to the homogeneous catalyst concentration level. Essentially, the Cu(II)-hydroperoxide complex would undergo an unimolecular decomposition at low amount of catalyst, releasing Cu(I), O₂•⁻, and H⁺. For higher Cu(II) levels, a bimolecular decomposition was postulated, in which Cu(I), H₂O₂, and O₂ would be produced. According to this author, in both the Fe(III)/H₂O₂ and the Cu(II)/H₂O₂ systems, the reduction of oxidized metal ion (i.e., Fe(III) and Cu(II)) by H₂O₂ (that is, the unimolecular decomposition of FeOOH²⁺ and CuOOH⁺ species) is the rate-limiting step for the production of reactive oxidants.⁵ Perez-Benito postulated the formation of O₂•⁻ in all the possible pathways, as intermediate together with OH• responsible for the chain-propagation steps:



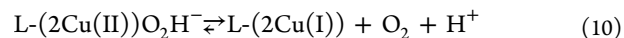
The radicals could react with the excess of H₂O₂, and at high Cu(II) concentrations, O₂•⁻ would decompose as follows:



In contrast, the inner-sphere reaction proposed by Masarwa et al. involved the reaction of L_m-Cu(I) with H₂O₂ to give L_{m-1}-Cu(I) (OOH⁻) and H⁺. This transient complex could

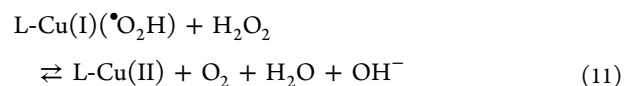
decompose in L_m-Cu(II), OH•, and OH⁻ or can react with an organic substrate like short-chain alcohols (ethanol, 2-propanol, or 2-butanol).⁹ It must be pointed out that no release of O₂ was considered in this mechanism.

Based on the work of Yamamoto and Kawanishi, another explanation for O₂ release could be the binding of H₂O₂ with two Cu(II), yielding the hydroperoxo-dicopper complex and the formation of O₂ by two-electron transfer, without the intermediate production of O₂•⁻:¹⁰

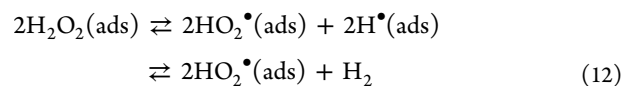


It has been reported that Cu(II) complexes can catalyze the decomposition of H₂O₂ only if the metal coordination sphere is not saturated by ligands,^{11,12} suggesting that the ternary L-Cu(II)-peroxo complexes are involved in the reaction.¹³

A slight modification of this "inner-sphere" mechanism involving the formation of the Cu(I) intermediate consists on the reaction between this intermediate and H₂O₂:^{14,15}

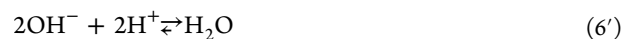
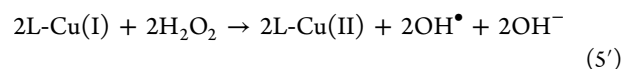
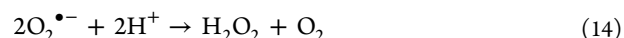
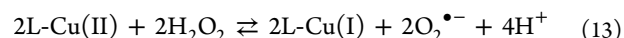


In this case, the OH• production is not considered. In this context, Lousada et al. have demonstrated that the presence of HO₂• at the surface of CuO catalysts can lead to the formation of a small amount of H₂ following



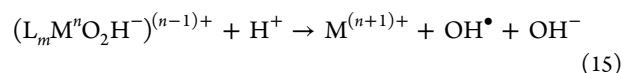
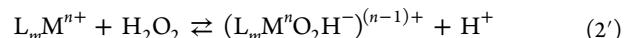
In addition, scavenging the intermediate product OH• leads to enhanced formation of H₂ and a decrease in the production of the main gaseous product O₂.³

An alternative outer-sphere reaction is consistent with the overall reaction stoichiometry:¹⁶⁻¹⁹



In the literature, the production of Cu(I) and O₂•⁻ has been considered both in the absence^{5,20,21} and presence of organic ligands.²²

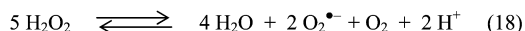
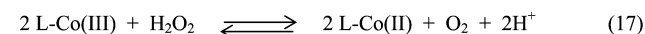
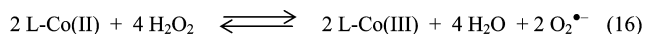
Regarding the so-called Fenton-like reaction (eq 5), Goldstein and Meyerstein emphasized that (in most transition-metal complexes with H₂O₂) it cannot proceed in aqueous solution via an outer-sphere electron-transfer mechanism because it would not be thermodynamically favored.²³ Thus, a transient complex between the catalyst and H₂O₂ must be the first step in this process, followed by different possible decomposition reactions dependent on the pH of the medium.



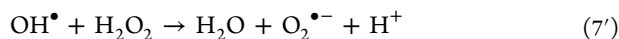
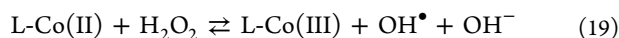
When Cu(I) is involved, L-Cu(I)O₂H⁻ could evolve to Cu(III) and H₂O at low pH values.

On the other hand, we also tested the activation of H_2O_2 catalyzed by $\text{Co(II)-poly(EGDE-MAA-2MI)}$ and $\text{Co(II)-poly(EGDE-DA)}$. Two probable mechanisms of H_2O_2 activation catalyzed by immobilized Co(II) described in the literature were consistent with our global previous results.

The most probable mechanism of activation involves the production of O_2 , $\text{O}_2^{\bullet-}$, and H^+ according to

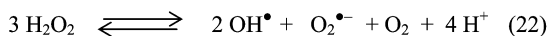
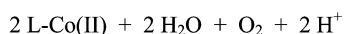
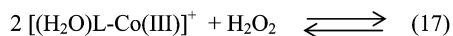
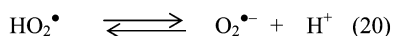
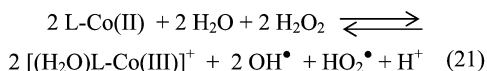


In this case, OH^\bullet was also detected as a product by spin trapping experiments. An explanation could be found by splitting the first step of the reaction as follows:



The stage of OH^\bullet degradation should be the slowest (even in the presence of the enzyme SOD), which would explain the observation of the $\text{DMPO}/\bullet\text{OH}$ signal.

Another speculative mechanism of H_2O_2 activation compatible with the production of O_2 and radicals would be as follows:²⁵



A third alternative must be considered. Agboola et al. presented spectroscopic evidence of the formation of cobalt intermediate species with catalytic activity ($[\text{L-Co(III)}(\text{OOH})]$), when Co(II) -based homogeneous catalysts were oxidized by H_2O_2 .^{25,26}

In this work we compare Co(II) - and Cu(II) -based catalysts for H_2O_2 activation, where the tested ligands are nonsoluble hydrogels derived from methacrylic acid and/or *N*-heterocycles, soluble polyelectrolytes, or their monomers. Here we present the performance of these catalytic species in the activation of H_2O_2 and the discussion of the possible mechanisms involved considering the free radicals and O_2 release, the coordinating functional groups, and the oxidation states of the metal ions in the active sites.

We consider that a study involving ligands of different nature represents a further step in the development of environmentally benign chemical processes, where the main scope is the replacement of current homogeneous oxidation procedures for either synthesis or environmental applications.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. The synthesis of polyampholytes and polyelectrolytes from ethylenglicol diglycidyl ether (EGDE), methacrylic acid (MAA), amines, and *N*-heterocycles and the obtainment of Cu(II) and Co(II) complexes were carefully described elsewhere.^{6,7,27–29} 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) and *poly(acrylic acid)* (*poly(AA)*) were purchased from Sigma–Aldrich. Superoxide dismutase (SOD) was from Biosidus (Buenos Aires, Argentina). H_2O_2 (30 wt %) was acquired from Merck (Darmstadt, Germany). Water was distilled with a FIGMAY glass apparatus (Córdoba, Argentina). All other reagents were of analytical grade.

2.2. Instruments. The *solid-state* nuclear magnetic resonance (*ss-NMR*) experiments were performed at room temperature in a Bruker Avance II-300 spectrometer equipped with a 4 mm MAS probe. The operating frequency for protons and carbons was 300.13 and 75.46 MHz, respectively. High-resolution ^{13}C solid-state spectra for the polymers were recorded using the ramp $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization and magic angle spinning (CP-MAS) sequence with proton decoupling during acquisition (SPINAL64) as in previous works.^{30,31} The spinning rate for all the samples was 10 kHz. The electron spin resonance (ESR) spectra were obtained at 20 °C using an in an X-band ESR Spectrometer Bruker EMX Plus (Bruker Biospin GmbH, Germany). Partial pressure of O_2 was measured with an Numak JPB-607A DO analyzer. Potentiometric measurements were made with a Hanna pH meter; the glass electrode was used for pH measurements, and a Pt working electrode (BASinc) with Ag/AgCl reference electrode (BASinc) were used for redox potential measurements. Each material was equilibrated in 1 M NaCl solution for 40 h, and the redox potential (E) was tested with a Pt electrode versus Ag/AgCl . X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic $\text{Mg K}\alpha$ radiation (300W, 15 kV, 1253.6 eV) for the analysis of the polymeric and Cu-polymer materials, as in previous works.^{6,31} A short acquisition time of 10 min was used to examine C 1s, Cu 2p, and Cu LMM XPS regions in order to avoid, as much as possible, photoreduction of Cu^{2+} species. For the Co-polymer complexes, the XPS spectra were collected with nonmonochromatic $\text{Al K}\alpha$ radiation (300 W, 15 kV, 1486.6 eV).³² The bulk cobalt content was obtained from the Co-hydrogel solids through X-ray Fluorescence (XRF) in an Advant XP⁺ Thermo Electron spectrometer.

2.3. Measurement of Free Radicals by ESR. The initial H_2O_2 concentration was set close to 60 mM. Higher concentration levels of H_2O_2 were expected to be less efficient in oxidative processes because of possible deleterious effect on the polymeric catalysts.³³ An amount of 0.0500 g of each complex was suspended in 50 mL of 60 mM H_2O_2 solution, and the production of free radicals was followed by ESR. Some experiments were also performed in the presence of SOD with an activity of 200 U mL^{-1} , which was added to the system before H_2O_2 .

Aliquots of 32 μL taken at different times of reaction were mixed with 16 μL of 3 M DMPO (spin trap), and the continuous wave (CW) ESR spectra of the DMPO spin adducts were recorded at 20 °C, 3 min after the end of incubation, in the X-band ESR spectrometer. The instrument settings and simulation conditions were reported previously by Lombardo Lupano et al.³³

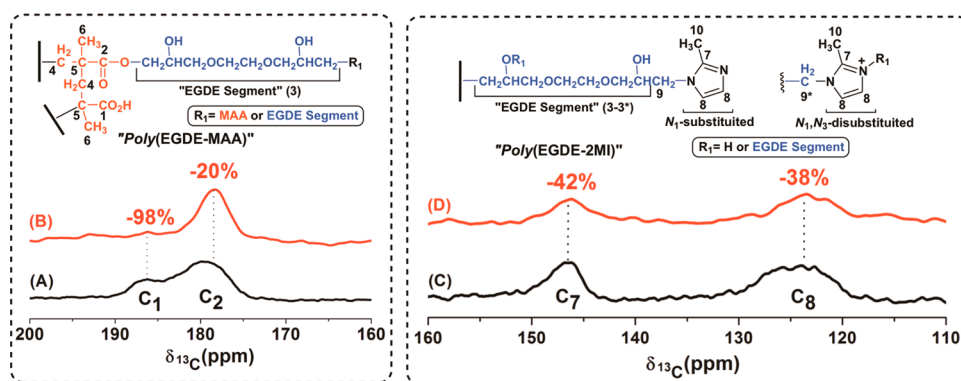


Figure 1. High-frequency regions of the ^{13}C CP-MAS spectra for *poly*(EGDE-MAA) (A), Co(II)-*poly*(EGDE-MAA) containing 1 mg Co(II) g^{-1} (B), *poly*(EGDE-2MI) (C), and Co(II)-*Poly*(EGDE-2MI) containing 35 mg Co(II) g^{-1} (D) with a contact time of 800 μs . In all the samples, the number of scans was 2000.

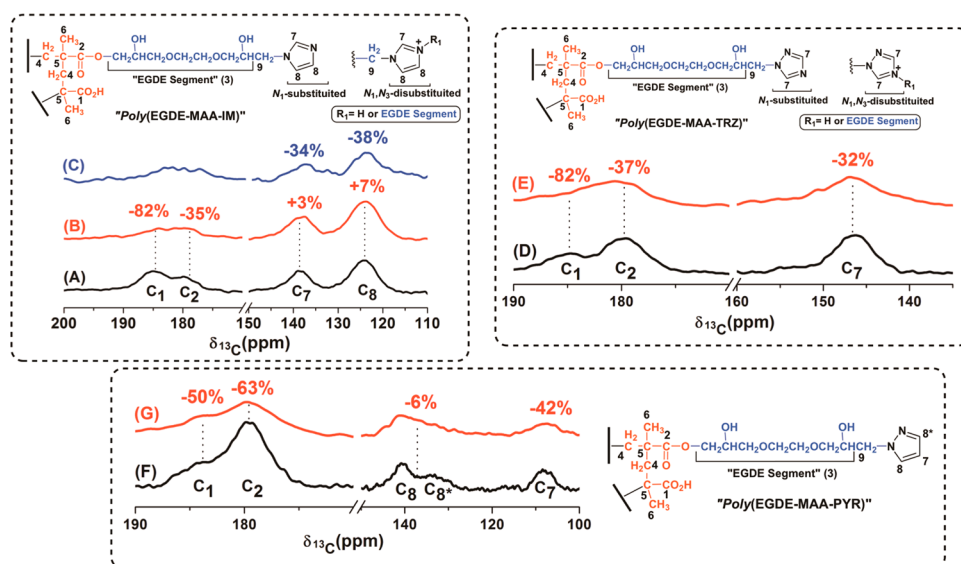


Figure 2. High-frequency regions of the ^{13}C CP-MAS spectra for *poly*(EGDE-MAA-IM) (A), Co(II)-*poly*(EGDE-MAA-IM) containing 2.6 mg Co(II) g^{-1} (B) or 23 mg Co(II) g^{-1} (C), *poly*(EGDE-MAA-TRZ) (D), Co(II)-*poly*(EGDE-MAA-TRZ) containing 18 mg Co(II) g^{-1} (E), *poly*(EGDE-MAA-PYR) (F) and Co(II)-*poly*(EGDE-MAA-PYR) containing 1 mg Co(II) g^{-1} (G) with a contact time of 800 μs . In all the samples, the number of scans was 2000.

3. RESULTS

The Cu(II) and Co(II) complexes were suspended in water, and spin trapping ESR experiments were performed to determine the eventual activation of dissolved O_2 . Then, when H_2O_2 was added, the release of O_2 , free radicals, and H^+ was monitored as a function of time. The complexes were analyzed by ss-NMR and XPS to understand the nature of the interaction between the transition-metal ion and each ligand and the changes undergone on H_2O_2 activation.

3.1. Solid-State Nuclear Magnetic Resonance Studies.

The ligands around the cobalt centers were studied first by ss-NMR techniques, because even when the Co(II) ions are paramagnetic, their study through EPR is limited to the system under study as well with the low temperatures required for the acquisition of the Co(II)-spectra with the concomitant reduction of the exchange of cobalt. On the other hand, the ss-NMR technique retrieves information on the ligands involved in the coordination of paramagnetic ions due to the enhancement in the relaxation behavior of different nuclei present in the polymer matrix (^1H , ^{13}C , ^{15}N , etc.). In particular, we have previously demonstrated that ^{13}C CP-MAS experi-

ments are effective for studying the preferences in the uptake of copper(II) ions at different concentrations of metal ions in polyelectrolyte and polyampholyte materials; however, some experimental conditions must be taken into account prior to setting the acquisition parameters, such as the contact time used in the cross-polarization steps in the CP-MAS experiments.^{27,30,34} Also, some other authors have used this strategy to study the coordination of mercury,³⁵ samarium,³⁶ and zinc³⁷ in polymer matrixes. In this work, the ^{13}C CP-MAS spectra were used to characterize the environment of the Co(II) ions after the uptake of the paramagnetic ions depending the different functional groups present in polymer materials. It is necessary to remark that this type of experiment is not quantitative, so the changes observed in a particular signal in the ^{13}C CP-MAS spectra will be used to predict which ligand is close to the Co(II) ions because of the enhancement in the paramagnetic relaxation that broadens the resonance signals of a particular segment of the polymer material, preventing their visualization.

First, the ^{13}C CP-MAS spectra for *poly*(EGDE-MAA) and its Co(II) complex containing 1 mg Co(II) g^{-1} were studied, and

the results are shown in Figure 1. The presence of Co(II) ions induced significant spectral changes; for example, C_1 and C_5 were particularly affected, because the Co(II) affects the carboxylic acid and the quaternary carbons of the polymerized methacrylic acid segment which is coordinated with the metal ion. Also, they are the closest carbons to Co(II); however, the C_4 and C_6 were practically unaltered (Figure 1 and Figure S1), because the distance to the Co(II) center is higher than in C_{1-5} , and that made the paramagnetic effects vanish.^{34,38} In addition, the carbonyl ester carbons (C_2) did not actively participate in the uptake of cobalt ions, and for that reason the signal is visualized with a reduction in its area of 15%. Furthermore, the C_3 belonging to EGDE segments increased the intensity of the signal, indicating that the cross-polarization from ^1H to ^{13}C was more effective than in the noncoordinated material because of the more ordered segments after the coordination of Co(II) which induced higher reticulation of the polymer chains in the A_{12} complex. Some similar results have been observed in polymers with cobalt ions at low levels of the metal ion.³³ In this work, a clear disappearance of the C_1 was evidenced with 98% of reduction in the NMR signal and just 15% in the reduction of C_2 , giving clear evidence that in this polymer material the carboxylic acid is the predominant ligand for cobalt ions (Figure 1).

Then, the monosubstituted imidazole ligands (1.4 mmol 2MI g^{-1} , 70%) of *poly*(EGDE-2MI) are available as possible ligands for Co(II) ions because the rest of them are N_1, N_3 -disubstituted with a permanent positive charge being not a ligand for Co(II).²⁹ In the Co(II)-*poly*(EGDE-2MI) containing 35 mg Co(II) g^{-1} , a reduction of 42 and 38% in C_7 and C_8 , respectively, is observed after the uptake of Co(II) ions, where not all the sites were occupied by a paramagnetic ion (Figure 1). Some other NMR signals such as C_{9-10} were affected because of the paramagnetic effect of cobalt ions (Figure S3).

Next, the Co(II)-*poly*(EGDE-MAA-IM) containing 2.6 or 23 mg Co(II) g^{-1} was analyzed, and the results are shown in Figure 2. The importance of the analysis in this material is that it carries both carboxylic acid and imidazole moieties (monosubstituted imidazole available for uptaking, 57%); therefore, the interaction and preferences can be qualitatively studied. At low levels of Co(II) adsorbed to *poly*(EGDE-MAA-IM) (2.6 mg Co(II) g^{-1}), the NMR lines corresponding to C_1 and C_2 were particularly reduced, being more affective on the C_1 than C_2 signals (Figure 2). In addition, C_{7-8} and C_3 were slightly increased, maybe as a consequence of a reticulation³³ induced by the uptake of Co(II) ions, as in the Co(II)-*poly*(EGDE-MAA) complex. Moreover, as the Co(II) ions increased in the polymer material (23 mg Co(II) g^{-1}), C_1 was strongly reduced together with an important decrease in the NMR signal of C_{7-8} , as a consequence of the direct interaction between the pyridine-type nitrogen of the monosubstituted imidazole with Co(II). Here again, the carbon imidazole signals did not completely vanish because not all the imidazole ligands are available for coordination, and some of them are unable to uptake the metal ions because they are N_1, N_3 -disubstituted, as in the Co(II)-*poly*(EGDE-2MI) complex. Furthermore, at the saturation level of Co(II) for *poly*(EGDE-MAA-IM) material, a general decrease of the hydrocarbon chain signal in the ^{13}C CP-MAS can be observed because of the dispersion of the paramagnetic ion in the Co(II)-polymer complex (Figure S2).

Moreover, the Co(II)-*poly*(EGDE-MAA-TRZ) containing 18 mg Co(II) g^{-1} with triazole as ligand shows a behavior similar to that of the materials with imidazole groups. An important

decrease in the resonance signal corresponding to C_1 is observed with a concomitant reduction of the signal at 147 ppm (C_7) and the carbonyl carbon of the ester groups (C_2). On the other hand, for the Co(II)-*poly*(EGDE-MAA-PYR) containing only 1 mg Co(II) g^{-1} pyrazole groups, both signals C_{1-2} were altered together with a reduction of 6 and 42% for C_{8-8^*} and C_7 , respectively, in comparison with the material without cobalt ions (Figure 2). Even when the maximum loading amount of Co(II) is lower than in the material bearing both carboxylic acid and imidazole or triazole group, these results show that the coordination in the polymeric materials bearing pyrazole does not involve the groups as much as in those bearing imidazole or triazole groups where the uptake of the Co(II) species is more significant. In the Co(II)-*poly*(EGDE-MAA-PYR), the carboxylic acid, ester carbonyl, and pyrazole groups were involved in the uptake of the cobalt ions at very low amounts of Co, being comparative different than the coordination modes in Co(II)-*poly*(EGDE-MAA) where only the C_1 signal was significantly affected. Specifically, only the C_1 resonance signal from the ^{13}C CP-MAS spectrum for the Cu(II)-*poly*(EGDE-MAA-PYR) vanished,³⁰ indicating that the ^{13}C CP-MAS can be used to follow different ligands involved in the uptake of both Cu or Co ions in an easy way.

3.2. Free Radical Production by Cu(II) Complexes.

3.2.1. Cu(II)-Complexes with Monomeric Ligands. Cu(II)- H_2O in solution did not produce any free radical detectable by our system and method. Instead, when H_2O_2 was added to this homogeneous system, the DMPO/ $\cdot\text{OH}$ adduct from $\text{OH}\cdot$ was observed (Figure S6). Cu(II) complexes with *N*-heterocycles or other monomers bearing $-\text{COO}^-$ groups were tested as O_2 or H_2O_2 activators by monitoring the ESR signal at 3500 G produced by DMPO adducts formed with the radical products.

Figure S6 presents the ESR spectra of different Cu(II) complexes with monomeric ligands in contact with water. Under these conditions, the dissolved O_2 could be activated by the complexes, releasing oxygenated free radicals. According to the chemical lability of the monomers involved as ligands in the complexes, there was a release of C-centered free radicals resulting from the deleterious effect of $\text{OH}\cdot$. Table S1 shows that the free radicals detected in the Cu(II)-MAA system were only C-centered because of the higher reactivity of the vinyl group. For other complexes, the $\text{C}\cdot/\text{OH}\cdot$ ratio remained in the 3.3–10 range, but in the Cu(II)-PYR system, the ESR signal was weak and the $\text{C}\cdot/\text{OH}\cdot$ ratio was close to 1.

After the addition of H_2O_2 to the different complex systems, $\text{OH}\cdot$ was detected in all cases, sometimes coexistent with paramagnetic species derived from the monomeric ligands (Figure S6 and Table S2). The concentration of this free radical reached the steady state with the activators Cu(II)-PYR or Cu(II)-2MI. The influence of $-\text{COO}^-$ as ligand in the H_2O_2 activation process became evident when Cu(II)-MAA (or Cu(II)-*poly*(AA)) was used as catalyst, because the amplitude of the DMPO/ $\cdot\text{OH}$ signal reached the highest value beyond 30 min of reaction (Table S2).

3.2.2. Cu(II) Complexes with Polymeric Ligands. The experimental evidence suggests that the free radicals' identity in H_2O_2 activation was directly related to the presence of Cu(II) in the catalytic site. When coordinated Cu(II) was used as catalyst in the activation, H_2O_2 produced $\text{OH}\cdot$. The pH value did not vary significantly at the time that partial pressure of O_2 increased together with the concentration of free radicals.^{6,7,28}

Table 1. ESR Signal Intensity Measured at 3500 G Corresponding to DMPO/•OH Adduct after H₂O₂ Addition to Cu(II)-Polymer; O₂ Partial Pressure Increase and Redox Potential (*E*) in Cu(II)-Polymer Systems and in Polymeric Systems, in the Absence of H₂O₂^a

Complex and <i>q</i> Cu(II)	signal amplitude at steady-state, and SD (×10 ⁶ A.U.)	maximal signal amplitude, SD (×10 ⁶ A.U.) and time	maximal average increase of O ₂ partial pressure (%)		redox potential (mV vs Ag/AgCl)	
			complex	ligand	complex	ligand
Cu(II)-H ₂ O	4.10 ± 0.10	—	—	—	—	—
Cu(II)- <i>poly</i> (EGDE-DA) 155 mg g ⁻¹	49.8 ± 3.4	—	164	13	+330	+233
Cu(II)- <i>poly</i> (EGDE-MAA) 1 mg g ⁻¹	6.90 ± 0.17	—	10	5	+357	+360
Cu(II)- <i>poly</i> (EGDE-2MI) 63 mg g ⁻¹	12.75 ± 0.84	—	n.d.	n.d.	n.d.	+363
Cu(II)- <i>poly</i> (EGDE-MAA-IM) 67 mg g ⁻¹	—	19.11 ± 0.40 (60 min)	55	3	+355	n.d.
Cu(II)- <i>poly</i> (EGDE-MAA-IM) 8 mg g ⁻¹	—	5.20 ± 0.25 (60 min)	n.d.	n.d.	n.d.	n.d.
Cu(II)- <i>poly</i> (EGDE-MAA-TRZ) 60 mg g ⁻¹	—	8.49 ± 0.56 (60 min)	23	7	+360	+343
Cu(II)- <i>poly</i> (EGDE-MAA-PYR) 38 mg g ⁻¹	3.5 ± 0.42	—	1	n.d.	+377	+368

^aS.D., standard deviation; n.d.: not determined.

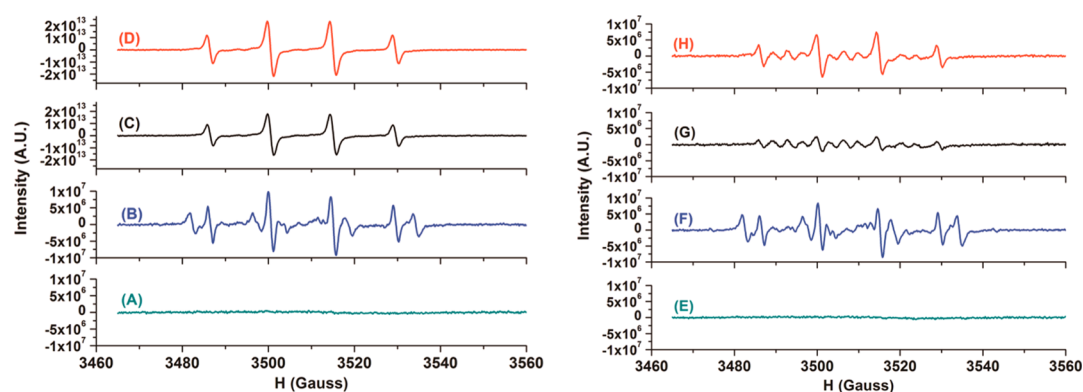


Figure 3. ESR spectra for DMPO in water (A), Cu(II)-*poly*(EGDE-DA) loaded with 155 mg Cu(II) g⁻¹ in water (B), and for the H₂O₂ activation by Cu(II)-*poly*(EGDE-DA) at reaction times of 10 min (C) or 30 min (D). ESR spectra for DMPO in water (E), Cu(II)-*poly*(EGDE-MAA-IM) loaded with 67 mg Cu(II) g⁻¹ in water (F), and for the H₂O₂ activation by Cu(II)-*poly*(EGDE-MAA-IM) at reaction times of 10 min (G) or 30 min (H).

Figure S7 and Table 1 summarize the experimental results of free radical trapping obtained from Cu(II)-polymer complexes. Figure S7 exhibits the spectra produced by aliquots of water in contact with Cu(II)-polymer: the adducts detected with DMPO indicated that dissolved O₂ could interact with the transition-metal ion and was activated by these complexes, releasing radical products of a different nature. These reactive oxygen species did not produce any detectable deleterious effect on methyl orange (azo dye) solutions.^{7,28}

Figure S7 exhibits the ESR signals obtained after H₂O₂ addition to Cu(II)-polymer systems. The kinetic profiles for free radical production catalyzed by Cu(II)-polymer systems varied with the nature of the ligands involved. These experiments were carried out maintaining fixed the mass of Cu(II)-polymer complex per volume of H₂O₂ solution, reason by which the amount of Cu(II) sites in the system varied with the material tested. In this way, the amount of free radicals generated depended on the density of catalytic sites (Table 1 and Figure S7).

When the efficiency of H₂O₂ activation by Cu(II)-polymer complexes was evaluated, it was observed that the main product

was OH• in most of cases, making a difference with the activation of dissolved O₂ (where the C•/OH• ratio was between 0.68 and 1.5). Nevertheless, the ESR signal intensity from O₂ activation with any Cu(II)-polymer complex was comparable (proportional) to the intensity of the signal from H₂O₂ activation with the same catalyst.

The highest production of DMPO/•OH adduct from activated H₂O₂ was achieved with Cu(II)-*poly*(EGDE-DA) containing 155 mg Cu(II) g⁻¹, followed by Cu(II)-*poly*(EGDE-MAA-IM) containing 67 mg Cu(II) g⁻¹, which also released other unidentified free radicals (Figure 3). In addition, the amount of Cu(II) bound to *poly*(EGDE-MAA-IM) clearly affected the kinetics and the efficiency on H₂O₂ activation.

The outstanding catalytic activity of Cu(II)-*poly*(EGDE-DA) could be related to the high density of Cu(II) sites in the hydrogel (Table 1), which is significantly higher than the Cu(II) uptake estimated for the other materials, in combination with the nature of the electron donor group from the polymer. In the spectrochemical series, -NH₂ is a strong-field ligand, whereas IM or -COO⁻ are somewhat weaker, which is

Table 2. Free Radical Species Obtained from H₂O₂ Activation by Co(II)-Polymer Systems, Average Molar Ratio, Average Amplitude of the Signal at 3488 G or Maximal Amplitude of the Signal and Time of Generation^a

complex	O ₂ ^{•-} average molar ratio and S.D.	OH [•] average molar ratio	signal amplitude at steady-state and SD (×10 ⁶ A.U.)	maximal signal amplitude and SD (×10 ⁶ A.U.) and time (min)
Co(II)-H ₂ O	1	–	15.41 ± 0.21	–
Co(II)-poly(EGDE-DA)	0.932 ± 0.022	0.068	–	4.14 ± 0.10 (10 min)
Co(II)-poly(EGDE-MAA)	n.d.	n.d.	9.64 ± 0.61	–
Co(II)-poly(EGDE-2MI)	0.912 ± 0.038	0.088	15.9 ± 2.8	–
Co(II)-poly(EGDE-MAA-IM)	0.961 ± 0.040	0.039	–	23.91 ± 0.10 (5 min)
Co(II)-poly(EGDE-MAA-TRZ)	0.912 ± 0.038	0.088	–	18.76 ± 0.16 (60 min)
Co(II)-poly(EGDE-MAA-PYR)	n.d.	n.d.	–	3.47 ± 0.10 (60 min)
Co(II)-poly(EGDE-MAA-2MI)	0.893 ± 0.045	0.107	–	2.97 ± 0.23 (10 min)

^aS.D., standard deviation; n.d., not determined.

consistent with the observations in these systems. Table S3 summarizes the results from a qualitative point of view.

The role of the *N*-heterocycle as electron donor in Cu(II) complexes became clear when the efficiency on H₂O₂ activation was studied. If TRZ was the *N*-heterocycle, the maximal Cu(II)-loading was similar to the values for IM- and 2MI-activators, but the signal amplitude of the DMPO/•OH adduct was lower.

The polyelectrolyte Cu(II)-poly(EGDE-MAA) presented the lowest density of catalytic sites. Nevertheless, the relative efficiency in production of OH[•] was higher than the performance of Cu(II)-poly(EGDE-MAA-IM) containing 8 mg Cu(II) g⁻¹. This particular behavior on H₂O₂ activation seemed to be directly related to the nature of the ligand.

Clearly, –COO⁻ as a Cu(II)-ligand resulted in better activator of H₂O₂ than *N*-heterocycles. For IM-polyampholytes at low Cu(II) uptake, the Cu(II) complexes were predominantly formed by IM residues.³⁰ It was demonstrated that –COO⁻ was also included as a ligand only when the amount of cation bound on the surface particles was close to saturation. In this way, the catalytic efficiency of Cu(II)-poly(EGDE-MAA-IM) was significantly enhanced in the condition of high Cu(II)-loading because of the contribution of –COO⁻.

At this point, another equivalent comparison can be made between Cu(II)-poly(EGDE-2MI) and Cu(II)-poly(EGDE-MAA-IM). The Cu(II) loading was similar in both cases, but the maximal H₂O₂ activation efficiency (even though high for both catalysts) seemed to be enhanced by –COO⁻ in the polyampholyte. When –PYR was the *N*-heterocycle in the polyampholyte, the Cu(II) uptake decreased by 40% and the radical response was comparatively poor.

The water-soluble Cu(II)-poly(AA) complex was also studied. When H₂O₂ was added to this homogeneous system, the identified free radicals were OH[•] and around 45.4 ± 9.6% of C-centered paramagnetic entities, exhibiting a performance comparable to Cu(II)-MAA in water.

Control experiments were made with the unloaded polymeric materials (without metal ion) which did not produce radical species in the absence of H₂O₂ (Figure S8). Unexpectedly, the DMPO/•OH adduct was detected after addition of H₂O₂, and the signal was monitored at 10 min of contact. It must be remarked that the activation of H₂O₂ by the Cu(II) complexes with the formation of OH[•] was more efficient in all cases when compared with the polymeric material

without metal ion. This H₂O₂ activation by polymers could be associated with the presence of *N* atom from electron-donor ligands and specially enhanced in the presence of pyrrolic-*N* atoms, which produces an electron-deficient environment and facilitates charge mobility.³⁹ According to previous reports, carbon materials with higher content of pyrrolic-*N* at the edges of graphene layers may exhibit improved charge mobility and donor–acceptor properties than pyridinic-*N* and graphitic-*N*.

In summary, the highest production of OH[•] was catalyzed by Cu(II)-poly(EGDE-DA), with –NH₂ being the strongest ligand. The amount of bound Cu(II) (and the density of catalytic sites) also affected the production level of free radicals. The nature of the *N*-heterocycle determined both the loading capacity of the material and the H₂O₂ activation efficiency. The –COO⁻ group resulted in better activator than IM, even in polymers with low density of Cu(II) sites.

The results obtained with catalysts involving monomeric ligands exhibited the main disadvantage of being chemically unstable in the reaction medium, producing C-centered free radicals, with the consequences of increasing the environmental impact together with the increasing difficulty of recovery and recycling. Nevertheless, the activation efficiency of homogeneous systems was relatively high, resulting from the high density of catalytic sites.

3.3. Free Radical Production by Co(II) Complexes.

Figure S9 shows the ESR spectra produced by DMPO in contact with an aliquot of the H₂O₂ solution activated by Co(II)-polymer systems at 10 min of reaction.

When the Co(II)–H₂O solution in the absence of H₂O₂ was analyzed, a weak signal from OH[•] was detected (Figure S9). After the addition of H₂O₂, the signal was only from O₂^{•-}, without any contribution from OH[•] (Table 2).

The Co(II) heterogeneous systems also exhibited poor activation of O₂. There was no evidence of O₂^{•-} formation. The only species detected by ESR was OH[•] when the ligands were polyelectrolytes such as in Co(II)-poly(EGDE-DA), but C-centered paramagnetic products appeared as the most abundant free radicals when polyampholytes formed part of the Co(II) complexes, such as in Co(II)-poly(EGDE-MAA-IM). The presence of OH[•] would be indicative of O₂ activation (perhaps a photosensitive reaction), which will be object of further research. The C-centered radicals would probably arise from ligand degradation.

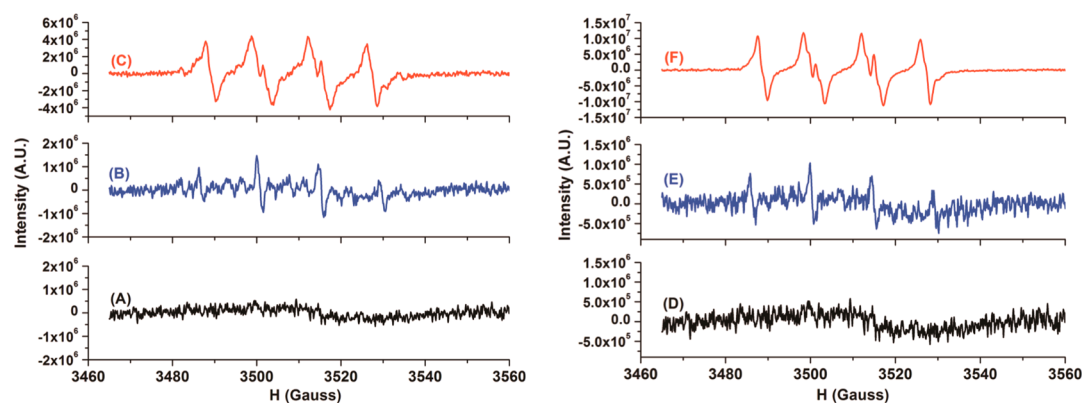


Figure 4. ESR spectra for DMPO in water (A), Co(II)-poly(EGDE-DA) loaded with 51 mg Co(II) g⁻¹ in water (B), and for the H₂O₂ activation by Co(II)-poly(EGDE-DA) at 10 min of reaction time (C). ESR spectra for DMPO in water (D), Co(II)-poly(EGDE-MAA-IM) loaded with 23 mg Cu(II) g⁻¹ in water (E) and for the H₂O₂ activation by Co(II)-poly(EGDE-MAA-IM) at 10 min of reaction time (F).

Instead, with H₂O₂ in the heterogeneous Co(II) systems, the simulated spectra were consistent with the presence of two radical species: DMPO/•OOH and DMPO/•OH adducts from O₂^{•-} and OH•, respectively. The presence of O₂^{•-} could be confirmed by the alteration of the ESR spectrum profile after superoxide dismutase addition (SOD).³³ This enzyme catalyzes the dismutation of O₂^{•-} to O₂ and H₂O₂, and the contribution of this species to the ESR signal diminishes or disappears.

The kinetic studies of activation of H₂O₂ by the different Co(II) complexes showed free radical production over 60 min of observation with a prevalence of O₂^{•-}. The molar ratio of the products (O₂^{•-} and OH•) was stable during the experiment (Table 2 and Figure S9).

The mean production of total free radicals (and the H₂O₂ activation efficiency) depended on the nature of the complex. The production of O₂^{•-} and OH• exhibited a steady state when H₂O₂ was activated by Co(II)-poly(EGDE-2MI). In this sense, the same behavior had been observed for the release of OH• by the Cu(II)-poly(EGDE-2MI)/H₂O₂ system (Tables 1 and 2). The lowest amount of free radicals was obtained with Co(II)-poly(EGDE-MAA-2MI)/H₂O₂, and the highest with Co(II)-poly(EGDE-MAA-IM)/H₂O₂ (Figure 4).

The presence of either a weak ligand like -TRZ or strong ligand like -IM in the polyampholyte significantly enhanced the release of O₂^{•-}. However, the role of -COO⁻ ligand as activator in the complex was not clear. The presence of -COO⁻ in the network together with -2MI inhibited the production of O₂^{•-}. In addition, the -TRZ acting as ligand from the polyampholyte resulted in a better activator for Co(II) than for Cu(II).

Regarding the nature of the products, the evidence indicates that OH• could be released either from the Co(II) site in the complex or from the N atoms in the ligands mentioned before.³⁹ In this sense, Liu et al. found high electrocatalytic activity in materials with high content of pyrrolic N and sites with low electronic density.

3.4. H₂O₂ Consumption and O₂ Production. In the evaluated systems involving Cu(II) or Co(II), the kinetic model of H₂O₂ consumption depended on the initial H₂O₂ concentration. For values of 0.1 mM, the kinetic order coincided with the order of reaction. When Cu(II)-poly(-EGDE-DA) is compared with Co(II)-poly(EGDE-DA), the Cu(II) complex presented a slower H₂O₂ consumption⁷ but a higher level of free radicals released.

The partial pressure of O₂ was determined before and after the addition of H₂O₂ to the different heterogeneous systems (Table 3). Here, the most efficient catalysts for molecular O₂

Table 3. O₂ Partial Pressure Increase after the Addition of H₂O₂ to Different Heterogeneous Systems with Co(II); the Same Information for Ligands in the Absence of the Cation; Redox Potential for the Heterogeneous Systems with Co(II) and for the Ligands, in the Absence of H₂O₂^a

complex	average maximal O ₂ partial pressure increase (%)		redox potential (mV vs Ag/AgCl)	
	complex	ligand	complex	ligand
Co(II)-poly(EGDE-DA)	221	13	+262	+233
Co(II)-poly(EGDE-MAA)	5	5*	+340	+360
Co(II)-poly(EGDE-2MI)	71*		+289	+363
Co(II)-poly(EGDE-MAA-IM)	13.5 (5 mM) ^b	3*	+320	n.d. ^c
	30 (100 mM) ^b			
Co(II)-poly(EGDE-MAA-TRZ)	4	7	+348	+343
Co(II)-poly(EGDE-MAA-PYR)	3	n.d.	+285	+368
Co(II)-poly(EGDE-MAA-2MI)	248	n.d.	+270	n.d.

^aThe relative standard deviation (R.S.D.) was lower than 20% except for the cases marked with one asterisk. ^bDifferent initial H₂O₂ concentrations. ^cNot determined.

release were poly(EGDE-DA) complexes with Co(II) and Cu(II) and Co(II)-poly(EGDE-MAA-2MI). Other complexes with 2MI or IM as ligands exhibited a good performance as activators. It can be inferred that the basic ligands contributed to enhance the O₂ production, being not dependent on the central metal ion.

In parallel, unexpectedly high O₂ to O₂^{•-} production ratio was found for Co(II)-poly(EGDE-DA)/H₂O₂ and Co(II)-poly(EGDE-MAA-2MI)/H₂O₂, the signal of DMPO/•OOH adduct being particularly low. The same high O₂ to OH• ratio was detected with Cu(II)-MAA with H₂O₂ in ethanol. In the first and the last case, it could be attributed to some loss of free radicals in reaction with the ligand matrix, supported by the fact that the DA-matrix is somewhat sensitive to O₂ species (becoming dark in time because of the N-oxidation process) and the vinyl group of MAA is reactive.

When Co(II)-poly(EGDE-MAA-2MI) was put in contact with H₂O₂, the production of O₂^{•-} was unexpectedly low. In this sense, a fraction of O₂^{•-} would not be released to the

Table 4. Cobalt Ion Content Determined by XRF and XPS Techniques; Co 2p Binding Energy Values, Spin-Energy Separation ($\Delta\text{Co}_{2p} = \Delta\text{Co}_{2p3/2-2p1/2}$), and Co LMM Auger Kinetic Energy Values for the Different Co-Complexes and after Being in Contact with a 60 mM H_2O_2 Solution

complex	Co wt % (XRF)	Co wt % (XPS)	Co 2p B.E. (eV)	ΔCo_{2p}	Co LMM KE (eV)
Co(II)- <i>poly</i> (EGDE-DA)	5.1	42.8	780.5 (58%)	16.0	767.8 (33%)
			782.6 (42%)	15.8	773.1 (67%)
Co(II)- <i>poly</i> (EGDE-DA)/ H_2O_2	1.6	20.7	780.0 (54%)	15.9	767.8 (27%)
			782.5 (46%)	16.0	773.1 (73%)
Co(II)- <i>poly</i> (EGDE-MAA-IM)	2.3	3.7	780.6 (40%)	14.9	766.7 (20%)
			782.6 (60%)	14.5	769.7 (80%)
Co(II)- <i>poly</i> (EGDE-MAA-IM)/ H_2O_2	0.6	2.2	780.5 (28%)	15.0	767.4 (62%)
			782.8 (72%)	15.6	770.0 (38%)
Co(II)- <i>poly</i> (EGDE-2MI)	3.5	37.7	780.3 (69%)	15.8	767.8 (33%)
			782.7 (31%)	15.3	773.1 (67%)
Co(II)- <i>poly</i> (EGDE-2MI)/ H_2O_2	0.6	9.0	780.0 (62%)	16.0	767.8 (27%)
			781.9 (38%)	15.5	773.1 (73%)
Co(II)- <i>poly</i> (EGDE-MAA-TRZ)	1.8	4.9	780.8 (70%)	15.6	767.8 (36%)
			783.3 (30%)	14.8	772.7 (64%)
Co(II)- <i>poly</i> (EGDE-MAA-TRZ)/ H_2O_2	0.7	2.5	780.6 (62%)	15.9	767.8 (41%)
			783.2 (38%)	15.3	772.3 (59%)
Co(II)- <i>poly</i> (EGDE-MAA-PYR)	0.3	1.5	780.5 (48%)	15.5	767.8 (58%)
			782.3 (52%)	16.2	773.1 (42%)
Co(II)- <i>poly</i> (EGDE-MAA-PYR)/ H_2O_2	0.1	<0.1	n.d. ^a	n.d.	n.d.
Co(II)- <i>poly</i> (EGDE-MAA)	0.1	0.9	780.9 (73%)	15.8	n.d.
			783.7 (14%)	14.8	
Co(II)- <i>poly</i> (EGDE-MAA)/ H_2O_2	<0.1	<0.1	n.d.	n.d.	n.d.

^an.d., not determined.

solution but involved in the formation of intermediate species ([L-Co(III) (OOH)]) on the catalytic surface.²⁶

The influence of $-\text{COO}^-$ was also observed in this experiment. The coordination sphere had been deeply studied before in Cu(II) complexes.³⁰ In Cu(II)-*poly*(EGDE-MAA-PYR) where the O_2 release was minimal, the atom ligands were 3N,1O or 2N,2O. Instead, IM- and TRZ- polyampholytes with a 55% and 22% O_2 increase had 1N,3O in the coordination sphere. In addition, Cu(II)-*poly*(EGDE-MAA-IM) after treatment with a large excess of H_2O_2 presented a change in the coordination sphere (3N,1O/4N) in parallel with the loss of catalytic activity.

Regarding Cu(II) monomer catalysts, the high production of gas could be associated with the higher content of metal ion per gram of complex (compared with polymeric complexes). Of course, these labile structures cannot be recovered and/or recycled as catalysts.

In Cu(II) systems, the release of H_2 together with the main gas O_2 could be possible in the context of the inner-sphere mechanism.³ This aspect was not explored and will be the topic of further research.

The structures without central metal also produced a small but detectable increase of dissolved O_2 , in parallel with the release of OH^\bullet . As was discussed elsewhere, the amount of free radical production catalyzed by *poly*(EGDE-DA) was not significant enough for an environmental application.⁷ Moreover, these nonsoluble ligands (free of metal ion) can be easily passivated by organic compounds, limiting the potential application.

3.5. X-ray Photoelectron Spectroscopy. The XPS technique is a valuable tool to analyze the chemical composition in the surface of the catalyst which is really in contact with the H_2O_2 solution. In addition, changes in the oxidation state of metal centers can be followed. The bulk and

superficial cobalt contents in the different Co(II)-polymer complexes were determined with XRF and XPS techniques, respectively, and are shown in Table 4. The quantitative information that it is obtained is related with only the surface of the material ($\sim 1\text{--}10\ \mu\text{m}$), taking into account the low penetration of X-rays in the XPS acquisition experiment.

In particular, the *poly*(EGDE-DA) and *poly*(EGDE-2MI) materials exposed a higher density of cobalt ions than the rest of the materials bearing in addition carboxylic acid moieties. In all the Co(II) complexes, after the addition of H_2O_2 solutions, an important release of cobalt ions was observed from both XPS and XRF results. This fact can be resolved with the addition of *poly*(EGDE-DA) hydrogel to the supernatant for an adequate treatment of the residues and reloading of the complexes with Co(II) to recover the catalytic efficiency.

It is well-known that the coordination of metal ions by different ligands produces an increase in the binding energy values for nitrogen or oxygen. In addition, the C 1s signals sense the effect of the metal ions with the concomitant shift to higher binding energy values, even when the metal ion was not directly bound to this element, but its presence affects the thermal stability of the chemical bonds of the entire network.^{6,7} For example, the N 1s spectrum was fitted using two Gaussian–Lorentzian peaks with energies of 398.7 and 400.9 eV for the *poly*(EGDE-MAA-IM). The first peak is assigned to the pyridinic nitrogen, whereas the second one is assigned to the pyrrolic nitrogen which is bound to the EGDE segments together with some protonated pyridinic nitrogens and N_1, N_3 -disubstituted nitrogens.⁶ With the uptake of cobalt ions, the pyridinic nitrogens bound to cobalt ions were shifted to 399.3 eV and the pyrrolic and N_1, N_3 -disubstituted nitrogens can be observed at 401.3 eV. Similar results were reported in Cu(II)-*poly*(EGDE-MAA-IM) complexes.⁶ However, for the *poly*(EGDE-DA) material, the N 1s spectrum was fitted with two

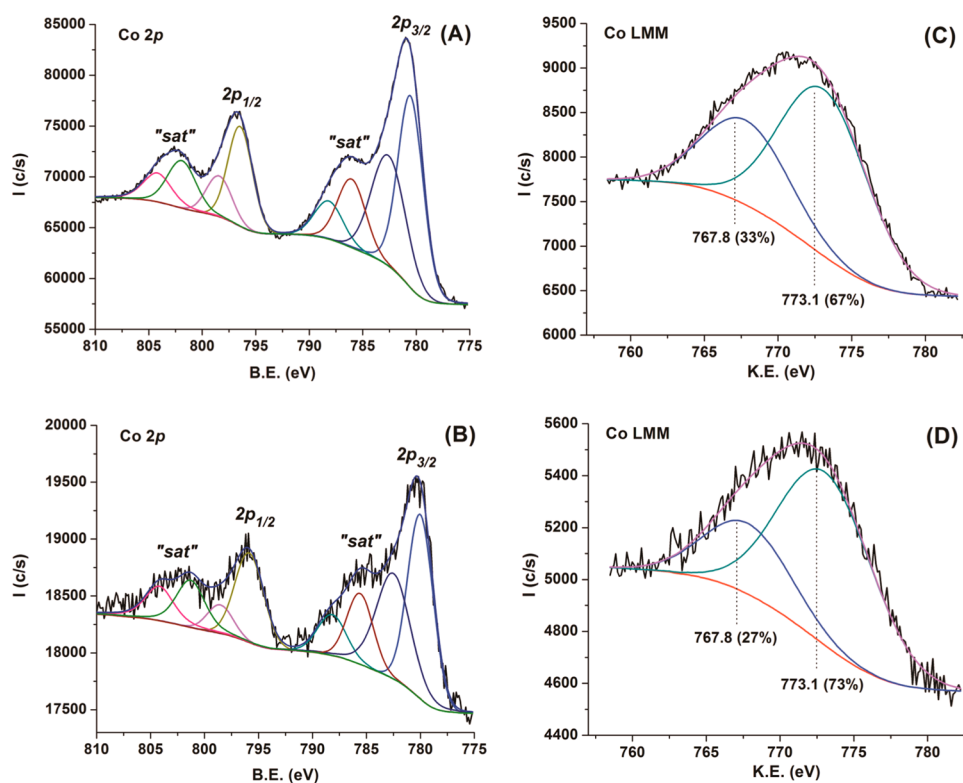


Figure 5. XPS spectra for the close-up Co 2p in the Co(II)-poly(EGDE-DA) containing 51 mg Co(II) g⁻¹ (A) and in the Co(II)-poly(EGDE-DA) incubated with H₂O₂ solution (B). Co LMM Auger spectra in the Co(II)-poly(EGDE-DA) containing 51 mg Co(II) g⁻¹ (C) and in the Co(II)-poly(EGDE-DA) incubated with H₂O₂ solution (D).

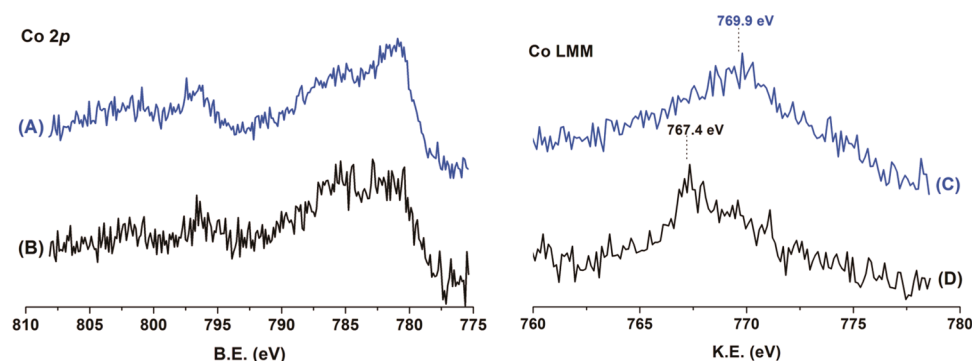


Figure 6. XPS spectra for the close-up Co 2p in the Co(II)-poly(EGDE-MAA-IM) containing 23 mg Co(II) g⁻¹ (A) and in the Co(II)-poly(EGDE-MAA-IM) incubated with H₂O₂ solution (B). Co LMM Auger spectra in the Co(II)-poly(EGDE-MAA-IM) containing 23 mg Co(II) g⁻¹ (C) and in the Co(II)-poly(EGDE-MAA-IM) incubated with H₂O₂ solution (D).

lines at 398.2 (83%) and 400.0 eV (17%) interpreted as nonprotonated and protonated nitrogens, respectively. With the coordination of cobalt ions, the N 1s core level spectrum showed a similar shape, but the two contributions were slightly shifted to higher binding energy values at 398.9 (85%) and 400.3 eV (15%), similar to those obtained with the coordination of copper ions at 398.1 (42%) and 400.1 eV (58%) but with different proportion of each nitrogen. The coordination of cobalt or copper ions did not produce an important shift to high binding energy value of the N 1s lines in polymer containing aliphatic nitrogen with sp³ hybridization³¹ as in the polymer containing heterocyclic units bearing nitrogen with sp² hybridization. However, the presence of the metal ion can be demonstrated and studied through their respective

photoelectron region in the polymer containing aliphatic nitrogen.

Related with the cobalt photoelectron region, the Co 2p core level and Co LMM Auger regions for all the Co(II) complexes were studied, and the results are shown in Table 4. In particular, the Co(II)-poly(EGDE-DA) containing the highest amount of cobalt per gram of polymer material was studied first with the aim to show the fitting used in the Co 2p and Co LMM Auger spectra (Figure 5).

The Co 2p spectrum of Co(II)-poly(EGDE-DA) displayed two major peaks for Co 2p_{1/2} at 780.5 (58%) and 782.6 eV (42%) together with a spin-orbit splitting ($\Delta\text{Co}_{2p} = \text{Co}_{2p_{1/2}} - 2p_{3/2}$) of 16.0 and 15.8 eV, respectively. The broad Co 2p line was indicative that there are different cobalt centers due to the difference in the coordination sphere of the metal ion. Also, the

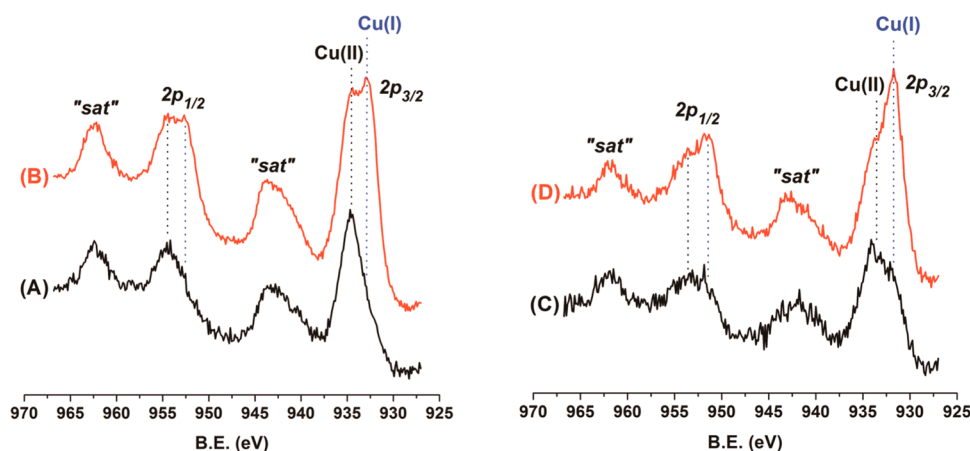


Figure 7. XPS spectra for the close-up Cu 2p in the Cu(II)-*poly*(EGDE-DA) containing 155 mg Cu(II) g⁻¹ with short (A) and long irradiation times (B) and for the Cu(II)-*poly*(EGDE-DA) incubated with H₂O₂ solution with short (C) and long irradiation times (D).

characteristic shakeup satellite signals denoted as “sat” are observed in Figure 5. Taking into account that Co(II) and Co(III) have almost similar 2p binding energies, they can be differentiated by the spin-orbit level energy spacing (ΔCo_{2p}), which is 16.0 eV for high-spin Co(II) and 15.0 eV for low-spin Co(III) for cobalt oxides.⁴⁰ However, there are not exhaustive studies performed in polymer or organic materials coordinated with cobalt ions involved in catalytic processes.^{25,41,42} For that reason, we focused the studies on the changes observed in the Co LMM Auger lines due to the fact that the spin-energy separation (ΔCo_{2p}) was close to 15.0 in Co complexes obtained from the incubation with CoSO₄ salt and the hydrogel materials in this work, being not in agreement with those observed in cobalt oxide materials for Co(II). It was not possible to observe difference in the photoelectronic and Auger region for the Co(II)-*poly*(EGDE-DA) after the addition of H₂O₂ in comparison with the unloaded materials (Figure 5 and Table 4), but for the Co(II)-*poly*(EGDE-MAA-IM) an important difference can be observed in the Auger Co LMM signals with the interaction with H₂O₂ (Figure 6 and Table 4). In the absence of H₂O₂, the Co LMM Auger signal appeared at 769.9 eV (80%) with a lower contribution at 766.7 eV (20%), while after the interaction with H₂O₂ it appeared at 767.4 eV (62%). The lower kinetic energy was associated with the Co(III), because the higher electrostatic potential of Co(III) slows the electron dissipation in comparison with Co(II). In the Co(II)-*poly*(EGDE-MAA-IM) it was possible to observe changes in the Auger line because the interconversion between Co(III) \rightleftharpoons Co(II) is slower than in the Co(II)-*poly*(EGDE-DA), explaining that even when the activation of H₂O₂ with the concomitant release of radical species took place, no Auger spectral changes can be observed because of the fast Co(III) \rightleftharpoons Co(II) step. This behavior was present only in the Co(II)-*poly*(EGDE-MAA-IM) polymer because in the rest of the Co complexes exposed to H₂O₂, the Co(III) species were not stabilized in order to be inferred through XPS studies.

Related with Cu-polymer complexes, we have previously demonstrated that Cu(I) was the intermediate in the activation of H₂O₂ in Cu(II)-*poly*(EGDE-MAA-IM) material.⁶ Specifically, the Cu 2p spectrum for the Cu(II)-*poly*(EGDE-DA) at short irradiation time showed only Cu(II) species at 933.3 (66%) and 935.3 eV (34%) with their corresponding shake up satellite signals, while at long irradiation time it presented both Cu(II) and Cu(I) (Figure 7). However, the presence of Cu(I)

was due to the photoreduction of Cu(II) induced at ultrahigh vacuum giving rise to a new signal at 932.6 eV for the Cu(II)-*poly*(EGDE-DA) complex in the absence of H₂O₂. With the activation of H₂O₂, the signal at 932.4 eV (26%) appeared at short irradiation time associated with the generation of Cu(I) because of the activation of H₂O₂ together with Cu(II) signals at 933.4 (23%) and 935.6 eV (51%), respectively. In this scenario, the Cu(I) centers were increased to 39% at long irradiation time as a consequence of the photoreduction of Cu(II) (Figure 7).

The particular combination of imidazole and carboxylic ligands in *poly*(EGDE-MAA-IM) materials particularly stabilized Cu(I) and Co(III) species involved in the catalytic process with H₂O₂ according to the XPS experiments.

3.6. Potentiometric Measurements. The redox potential (E) of a Pt electrode (vs Ag/AgCl) immersed in each heterogeneous system was measured in the absence of H₂O₂. The solid phase could be Cu(II) complexes, Co(II) complexes, or ligands.

Cu(II) complexes and most of the systems involving metal-free polymers (except *poly*(EGDE-DA)) in suspension, exhibited an E value around +360 mV vs Ag/AgCl. The E value for a H₂O₂ solution was +350 mV vs Ag/AgCl.

IM has a well-known tendency to increase the redox potential of the Cu(II)/Cu(I) couple, whereas ligands containing -NH₂ tend to decrease it.⁴³ In fact, Cu(II)-*poly*(EGDE-DA) exhibited a lower E , when compared with the Cu(II) complexes with IM-derived ligands, suggesting that E was associated with the presence of Cu(II)/Cu(I) mixture (perhaps involving traces of Cu(I)).

Lower redox potential values for the catalysts should be associated with higher production of OH[•] in H₂O₂ activation experiments.⁴⁴ In fact, the lowest redox potential corresponded to Cu(II)-*poly*(EGDE-DA) system, which was associated with the highest OH[•] production (Table 1) and the highest O₂ release when H₂O₂ was added.

In addition, two groups of systems could be observed for Co(II)-catalysts: one related to 2MI, DA, and PYR-bearing polymers developing an E close to +270 mV and another group around +330 mV related to the highest free radicals production level.

From another point of view, the complexes Co(II)-*poly*(EGDE-2MI) and Co(II)-*poly*(EGDE-MAA-PYR) were associated with E values 60–70 mV lower than the E generated

by their respective ligands. In those cases, the redox couple involved could be Co(III)/Co(II).

Then, when H₂O₂ was added to the heterogeneous systems Cu(II)-*poly*(EGDE-MAA-IM) and Co(II)-*poly*(EGDE-MAA-PYR), the *E* value increased to +400 mV at equilibrium. Instead, when H₂O₂ was added to soluble Cu(II)-H₂O, the *E* moved from +374 to +350 mV. In these last experiments, the *E* was determined by O₂/H₂O₂ redox couple, considering both the identity and amount of the compounds involved.

4. DISCUSSION

4.1. Oxidation State of Metal Ions in Complexes. The Cu(II) complexes designed by our group had been used as heterogeneous catalysts for H₂O₂ activation and MO decoloration.^{7,28}

The catalytic properties of Cu(II)-*poly*(EGDE-MAA-IM) had been confirmed by recycling the solid in six consecutive experiments. In addition, several changes in XPS spectra of Cu(II)-*poly*(EGDE-MAA-IM) had been detected after the treatment with H₂O₂ together with the predominant presence of Cu(I) observed in Auger spectrum.⁶

Another evidence of Cu(I) formation had been found in the ESR measurements of Cu(II)-*poly*(EGDE-MAA-IM) containing 67 mg Cu(II) g⁻¹ after treatment with H₂O₂:³⁰ the paramagnetic centers of Cu(II) were reduced mainly to diamagnetic centers of Cu(I); only 5% of the original Cu(II) centers remained in the catalyst. The atoms of the ligands involved in the coordination sphere in Cu(II)-*poly*(EGDE-MAA-IM) containing 67 mg Cu(II) g⁻¹ were 1N,3O, and changed to 3N,1O/4N after treatment with H₂O₂. In addition, ESR parameters after H₂O₂ addition were similar to those obtained with Cu(II)-*poly*(EGDE-MAA-IM) containing 8 mg Cu(II) g⁻¹, in which the main ligand was IM according to both ss-NMR and EPR results.³⁰ Cu(II)-*poly*(EGDE-DA) was also the object of study by XPS. In this case, the activation of H₂O₂ rendered 26% of Cu(I) species together with 74% of Cu(II) according to the Cu 2p spectra (Figure 7).

When XPS spectra were obtained for Co(II)-*poly*(EGDE-MAA-IM) before and after treatment with H₂O₂, strong evidence supported the formation of Co(III) coexistent with Co(II) by action of H₂O₂. Other Co(II) complexes did not evidence the coexistence of the oxidation states involved in the catalytic mechanism. In other words, the interconversion between Co(III) and Co(II) in Co-*poly*(EGDE-MAA-IM)/H₂O₂ was slower than in the other catalysts.

In summary, this *poly*(EGDE-MAA-IM) acting as ligand stabilized particularly Co(III) and Cu(I) involved in the corresponding catalytic cycles. *poly*(EGDE-DA) did not particularly stabilize any of the copper states of valence. Instead, the other ligands seemed to stabilize preferentially Co(II) and Cu(II).

4.2. Relevance of the Nature of the Ligands. A comparison was made between different catalytic systems, with the aim of elucidating the role of ligands and their nature in the activation of H₂O₂. We worked with a group of materials complexed with Cu(II) or Co(II), bearing -COO⁻ groups, N-heterocycles, amines, even polymeric, or monomeric. It was expected that, according to the group involved in the coordination sphere, the catalytic efficiency was also affected by the density of active sites on the catalyst. In this way, we could analyze the influence of each factor (ligand nature, and cation loading) on the efficiency and the contribution of both factors simultaneously.

From data fitting and simulations, it was observed that certain polymeric materials (without metal ion) activated H₂O₂, generating OH[•] and a minor quantity of O₂. For Cu(II) complexes, the same products were detected on H₂O₂ activation. The ESR studies for OH[•] production demonstrated that the nature of the ligand in the complex affected the amount of free radical detected. In some cases, C-centered free radicals were also produced when the ligand itself was susceptible to oxidation.

For Co(II) complexes, the H₂O₂ activation generated O₂^{•-}, OH[•], and O₂. The information obtained from the experiments revealed that the O₂^{•-} to OH[•] ratio was stable in time, with net prevalence of O₂^{•-}. Here, it was considered that OH[•] could arise from the complex activity and/or from the polymeric matrix activity.

It is known that the ligands involved in each complex can affect the copper or cobalt reactivity and/or the amount of product released through three possible mechanisms:⁴⁴ by decreasing the Cu(II)/Cu(I) or Co(III)/Co(II) redox potential (*E*) at the expense of the "Fenton-type" reaction; by scavenging the OH[•]/O₂^{•-} radicals released to the solution; or by acting as OH[•]/O₂^{•-} inactivating ligands. This last case refers to those organic compounds that form complexes and keep an adequate redox potential but inactivate the free radicals as soon as they are formed by producing innocuous metabolites.

It was evident that in Cu(II)-*poly*(EGDE-MAA-IM)/H₂O₂, the OH[•] increased in parallel with Cu(II) loading (Table 1). Cu(II)-*poly*(EGDE-MAA), Cu(II)-*poly*(EGDE-MAA-IM), and Cu(II)-*poly*(EGDE-MAA-TRZ) exhibited *E* values between +355 and +360 mV, but the first complex had lower density of Cu(II) sites producing lower amounts of OH[•] and O₂.

In our cases, the *E* did not result in a highly sensitive variable to evaluate the performance of the catalysts because the *E* range for Cu(II) complexes presented an amplitude of only 50 mV, and for Co(II) complexes it was lower than 90 mV. Nevertheless, the highest *E* value was obtained with Cu(II)-*poly*(EGDE-MAA-PYR), which was the less efficient Cu(II)-catalyst, and the lowest *E* value was for the best catalyst Cu(II)-*poly*(EGDE-DA).

When the ligands were monomers or soluble *poly*(AA), the density of catalytic sites was higher. The efficiency in OH[•] production improved if -COO⁻ group or PYR was involved. Instead, Cu(II)-2MI exerted an apparent inhibitory effect compared with Cu(II)-H₂O dissolved in water. In the particular case of 2MI monomer, there was no support to consider it as an inactivating ligand; the ESR evidence was only informative about a lower release of free radicals, and the spectra fitted well to DMPO/•OH adduct. So, 2MI could be blocking the available sites on copper coordination sphere, where H₂O₂ should interact.^{44,45}

From the visual inspection and from the atypical ESR spectra, it was evident that some small ligands were more sensitive than polymers to the deleterious effects of free radicals. MAA and PYR were particularly labile to the products (or to the high amount of them) and became the target of these reactive molecules; thus the ESR spectra resulted from the contribution of different paramagnetic entities.

4.3. Insight into O₂ Activation. The release of free radicals from O₂ activation was not observed when Cu(II)-H₂O or the ligands were tested as catalysts. Most of the Cu(II)-monomer or Cu(II)-polymer complexes exhibited activity, except Cu(II)-*poly*(EGDE-MAA-IM) containing 8 mg Cu(II) g⁻¹ and Cu(II)-*poly*(EGDE-MAA) with 1 mg Cu(II) g⁻¹ where

the density of metal ions was too low. The reactive oxidation species detected was OH^\bullet , together with C-centered free radicals resulting from the strong deleterious effect of the radical on the organic structure of these materials.

Curiously, $\text{Co(II)-H}_2\text{O}$ and Co(II)-polymer complexes in the presence of O_2 also released OH^\bullet , instead of $\text{O}_2^{\bullet-}$, but the amount of free radicals detected was significantly lower than for Cu(II) systems. The organic ligands in the presence of O_2 released some amount of C-centered paramagnetic species, and the most affected by the radicals were the polyampholytes.

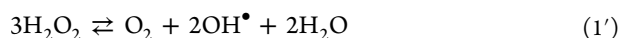
Previous studies of azo dye decolorization using Cu and Co catalysts indicated that the dissolved O_2 was not an efficient oxidant itself. In fact, the dyes just adsorbed on the catalyst and their concentration reached equilibrium, indicating that the dissolved O_2 was not reacting with these solutes.

The mechanism of O_2 activation by Cu(II) could involve Cu(I) , as reported elsewhere.⁴⁶ Regarding Co -catalysts, upon O_2 addition most Co(II) complexes form kinetically inert low-spin Co(III) terminal superoxide or μ -peroxide compounds that are active only in catalysis by addition of a coreductant (often, an organic ligand with redox properties).⁴⁷ Hanna et al. reported the oxidation of DMPO to the $\text{DMPO}/\bullet\text{OH}$ adduct by Co(II) and ethylenediamine when O_2 was present. In that case, the evidence strongly suggested a direct interaction between DMPO and the cobalt-ethylenediamine complex in solution.⁴⁸

Li et al. reported that the $\text{Co(II)} (\text{HCO}_3^-)$ (*o*-aminophenol) complex reacts with O_2 to give Co(III) and $\text{O}_2^{\bullet-}$, which further reduces to O_2^{2-} , because amino and polyamino are important ligands for Co(II) ions in solution, facilitating the electron transfer.⁴² They pointed out that the system can produce OH^\bullet radicals, and that the coordinating organic molecules play an important role in the rate of OH^\bullet formation. In our case, a detectable amount of OH^\bullet was released by the nonsoluble catalysts to the solution and then detected by spin trapping with DMPO. Instead, no evidence of free $\text{O}_2^{\bullet-}$ was obtained.

4.4. Possible H_2O_2 Activation Mechanisms. **4.4.1. $\text{Cu(II)-Polymer Systems}$.** The $\text{Cu(II)-polymer}/\text{H}_2\text{O}_2$ heterogeneous systems produced gas bubbles and OH^\bullet free radicals detected by spin trapping experiments with DMPO. The pH value did not vary significantly at the time that the partial pressure of O_2 increased together with the concentration of free radicals. The Cu(I) species were detected together with Cu(II) by XPS studies of $\text{Cu(II)-poly(EGDE-MAA-IM)}$ and of $\text{Cu(II)-poly(EGDE-DA)}$ after activation of H_2O_2 , being more abundant the Cu(II) content in the last case. Here there is a parallelism with the results from the experiments performed in homogeneous phase by Ozawa and Hanaki.⁴⁹ In this sense, Pecci et al. mentioned that H_2O_2 and Cu(II) interact producing free O_2 in two distinct ways, related to the coordination state of Cu(II) and of formed Cu(I) : if Cu(I) had been strongly stabilized by the ligand, $\text{O}_2^{\bullet-}$ would have been intermediate in the release of O_2 and H^+ .⁸

Based on previous studies on H_2O_2 activation catalyzed by copper complexes,^{6,28} a possible reaction could be considered:



There are two mechanisms for this stoichiometry: the inner-sphere mechanism and the outer-sphere mechanism. The outer-sphere reaction presented in the Introduction is consistent with the reaction stoichiometry.^{16–19}

The inner-sphere mechanism involves the formation of $\text{L-Cu(I)}\bullet\text{O}_2\text{H}$. According to Pecci et al., this intermediate reacts

with H_2O_2 releasing O_2 and OH^\bullet .⁸ This radical is expected to react with the excess of H_2O_2 or to dimerize regenerating H_2O_2 .

In our ESR studies with DMPO, the $\text{O}_2^{\bullet-}$ adduct was not detected in the reaction medium when nonsoluble Cu(II) complexes with different types of ligands were used. Thus, we simulated spectra of mixtures of $\text{DMPO}/\bullet\text{OH}$ and $\text{DMPO}/\bullet\text{OOH}$ adducts with different molar ratios. It was observed that the $\text{DMPO}/\bullet\text{OOH}$ to $\text{DMPO}/\bullet\text{OH}$ ratio must be greater than 0.25 to be estimated by deconvolution.

We also observed that the ligands themselves can induce OH^\bullet release in parallel, even in the absence of central metal ion, but the deleterious effect of OH^\bullet on target molecules such as azo dyes was obtained only when the Cu(II) or Co(II) complexes with functionalized polymers catalyzed the H_2O_2 activation.^{7,28}

Both inner and outer sphere mechanisms are consistent with our overall experimental results because stable pH is predicted, together with the release of O_2 and of OH^\bullet via a "Fenton-like" reaction between Cu(I) and H_2O_2 . The soluble intermediate $\text{O}_2^{\bullet-}$ expected for the outer sphere mechanism was not detected by our ESR method, constituting preliminary evidence that would support the first mechanism against the second. However, the intermediate species considered in the inner-sphere mechanism could neither be evidenced by ESR in these heterogeneous systems. For that reason, H_2O_2 was activated by soluble Cu(II)-poly(AA) and the whole homogeneous system was monitored by ESR. The simulated spectra as a function of time represented OH^\bullet (molar ratio 0.48) and two C-centered radical species, probably from partial degradation of the ligand poly(AA) . No changes in chemical shift of ESR signal were observed when compared with $\text{DMPO}/\bullet\text{OH}$; the value resulted just as the average (3508 ± 1 G) for all the Cu(II) systems tested by us. Instead, departures from 7 G were detected elsewhere between $\text{DMPO}/\bullet\text{OH}$ adducts and ligand- Cu(II) -radical complexes.²² In this way, there was no direct evidence of an inner-sphere mechanism involved in this catalytic H_2O_2 activation.

Cu(II)-PYR also turned out to be a homogeneous catalyst after H_2O_2 was added. Even though the complex was dissolved and changed from blue to green, the chemical shift of the ESR signal remained on 3509 G. The simulated spectra obtained over the reaction time fitted to $\text{DMPO}/\bullet\text{OH}$ (average molar ratio 0.90 ± 0.08) and a nonidentified radical species which now reinforced the hypothesis of a intermediate involving the active site and oxygen.

The necessary presence of a certain amount of Cu(I) to support these mechanisms was detected by XPS when $\text{Cu(II)-poly(EGDE-MAA-IM)}$ ⁶ or $\text{Cu(II)-poly(EGDE-DA)}$ were used as catalysts. These measurements were made on samples previously treated with H_2O_2 after a relatively long contact period in which H_2O_2 was consumed. In this condition of H_2O_2 depletion, the slowest stage of this catalytic cycle would determine the final form of the catalyst in the analyzed sample. Actually, Cu(I) needs H_2O_2 for its conversion to Cu(II) . According to XPS and Auger results, the conversion of L-Cu(I) to L-Cu(II) could be the slowest step in this case, so that L-Cu(I) would accumulate on H_2O_2 consumption, to finally predominate over Cu(II) in the analyzed material.

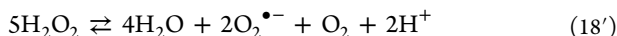
In the tested activating systems involving either Cu(II) or Co(II) , the kinetic model of H_2O_2 consumption depended of the initial concentration level.^{7,28} For values of 0.1 mM H_2O_2 , the kinetic order coincided with the reaction order. If we compare $\text{Cu(II)-poly(EGDE-DA)}$ with $\text{Co(II)-poly(EGDE-DA)}$

DA), the Cu(II) complex presented slower H₂O₂ consumption and a higher level of free radicals released. Here, the possibility of some H₂O₂ reformation through the course of reaction should be considered.¹³ Where available, O₂^{•-} could dismutate to H₂O₂ and O₂.

The “Fenton-like” reaction described above (eqs 5 and 19) is supported by many authors in the literature. However, in the case of copper and under some conditions, the true active oxidant is the Cu(III) state, which is considerably less reactive than OH[•].⁹ In our systems, Cu(III) was not evidenced.

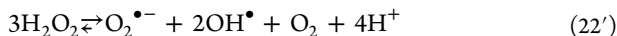
4.4.2. Co(II)-Polymer Systems. Two probable mechanisms of H₂O₂ activation catalyzed by immobilized Co(II) described in the literature were consistent with our global results.

The most probable mechanism of activation involves the production of O₂, O₂^{•-}, and H⁺ according to the following overall reaction:²⁴



The ESR spectra also evidenced the presence of OH[•] as a minor product of the reaction and as the main product after the addition of SOD.^{7,28} The OH[•] detected in these experiments could actually be released by the polymeric matrix (Table 2). In fact, when H₂O₂ was added to soluble Co(II)-H₂O, the signal belonged to only the adduct DMPO/•OOH, and no contributions of OH[•] were observed. Another explanation for the detection of OH[•] can be found by splitting the first step of the reaction, meaning that this species would be an intermediate stable enough to be detected.

The other speculative mechanism of H₂O₂ activation compatible with the production of O₂ and radicals would lead to the next overall reaction:²⁵



This second possible mechanism predicts molar fractions equal to 0.33 and 0.67 for the radical species O₂^{•-} and OH[•], respectively, which is not consistent with the experimental evidence of a O₂^{•-} preponderance (Table 2) in all the observed cases.

A third alternative is related to the formation of cobalt intermediate species with catalytic activity ([L-Co(III) (OOH)]), when Co(II)-based homogeneous catalysts are oxidized by H₂O₂.^{25,26}

Our experimental results of XPS with Co(II)-poly(EGDE-MAA-IM) support the formation of Co(III), in coincidence with the proposed mechanisms and also with these hypothetical [L-Co(III) (OOH)] intermediate species. It must be taken into account that the surfaces of these catalysts are heterogeneous in terms of chemical composition. The different probable combinations of ligands in the coordination sphere of Co(II) in these systems would explain some extent of heterogeneity in redox potentials (*E*) of the active sites (Table 3) and thus the eventual coexistence of the proposed mechanisms.

In the heterogeneous systems studied here, either the possible intermediate [L-Co(III) (OOH)] or the free radicals could eventually react with organic substrates. In this context, the possible formation of intermediate species on the surface of the particles was studied. For Co(II)-poly(EGDE-MAA-2MI), there was not practical evidence of the cobalt intermediates with catalytic activity on the particles surface in contact with H₂O₂. Instead, Co(II)-poly(EGDE-DA) activity on an azo-dye oxidation could not be explained only by the action of O₂^{•-} and OH[•] in solution, giving place to the hypothesis of intermediates on the catalytic surface.

5. CONCLUSIONS

In this work we presented the quali-quantitative results of H₂O₂ activation studies employing different systems, homogeneous and heterogeneous, and probable mechanisms were proposed on the basis of spectroscopic evidence, information about the specialized literature, and previous experiments performed by our group.

When H₂O₂ was activated by the Cu(II)-H₂O homogeneous system, OH[•] was identified. Though this indicated certain activity of Cu(II) in solution, the free radical production resulted in low respect to the response of Cu complex systems based on organic ligands.

When Cu(II)-poly(EGDE-MAA-IM) or Cu(II)-poly(EGDE-DA) systems were tested on H₂O₂ activation, the coexistence of Cu(II) and Cu(I) would be evidence that the complex is actually a catalyst acting at trace levels and recycling between two oxidation states. Other Cu complexes only exhibited Cu(II) after activation, possibly due to differences in step reaction rates which prevented Cu(I) accumulation. In the same way, Co(II) and Co(III) could be detected only on H₂O₂ activated by Co(II)-poly(EGDE-MAA-IM).

The set of experimental evidence was used to postulate possible mechanisms of H₂O₂ activation for each complexed cation. For Cu(II) complexes, the proposed models involve the species Cu(II)/Cu(I), OH[•], and O₂. In the literature, two large groups of possible mechanisms are reported: the inner-sphere and the outer-sphere. The inner-sphere requires the formation of intermediate L-Cu(II) (OOH), L-Cu(I) (•O₂H), or O₂ production from a hydroperoxo-dicopper complex, but there was no direct evidence of intermediate species in the tested systems. The proposed mechanism of outer-sphere involves O₂^{•-} as intermediate species, which was not detected. It could be a mixture of both types of mechanisms due to the heterogeneity of the sites in each material.

For Co(II) complexes, there are different models reported in the literature in which the Co(II)/Co(III) species participates besides O₂^{•-}, OH[•], O₂, and H⁺. The formation of cobalt intermediate species like L-Co(III) (OOH) with catalytic activity in the particles could not be irrefutably demonstrated, even if some evidence of its presence could be gathered.

The performance of these heterogeneous systems on H₂O₂ activation was evaluated in terms of the production of reactive species. The density of active catalytic sites in each Cu complex turned out to be a significant variable determining the efficiency of heterogeneous catalysis, with Cu(II)-poly(EGDE-DA) being the best activator. The relevance of -NH₂ from DA as ligand of Cu(II) affected both the uptake capacity of the polymer and the enhancement of activation rate.

In the Co(II) systems, the free radical release did not necessarily correlate with O₂ production. The highest levels of O₂^{•-} were obtained with Co(II)-poly(EGDE-MAA-IM), and the highest levels of O₂ came from Co(II)-poly(EGDE-MAA-2MI), both polyampholytes of similar nature, where the presence of Co(II) and Co(III) was clearly evidenced. Surprisingly, the lowest O₂^{•-} production was from Co(II)-poly(EGDE-MAA-2MI).

Cu(II) and Co(II) monomer catalyst were proven to be efficient H₂O₂ activators because of the high density of active sites, being strongly sensitive to free radical attack. The polymeric ligands also induced H₂O₂ activation but in a less efficient way than the corresponding complexes.

The Cu(II) and Co(II) complexes were able to activate dissolved O₂, producing OH• independently of the metal ion involved in the catalytic site. The C-centered paramagnetic species detected by ESR resulted from the deleterious effect of OH• on the structure of the organic ligands involved.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b10957.

Details concerning ss-NMR, XPS, ESR, and free radical production by different Cu(II) and Co(II) systems (PDF)

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Notes

The authors declare no competing financial interest.

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