

# Homogeneous versus heterogeneous catalytic reactions to eliminate organics from waste water using H<sub>2</sub>O<sub>2</sub>

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Homogeneous (Cu<sup>2+</sup> ions) and heterogeneous (Cu<sup>2+</sup>-pillared clay) Fenton-like catalysts have been compared in the conversion of *p*-coumaric acid. The performances of the two classes of catalysts are similar for an analogous amount of copper, but there are some relevant differences in terms of (i) the presence of an induction time, (ii) the turnover frequency, (iii) the efficiency in the use of H<sub>2</sub>O<sub>2</sub>, (iv) the initial attack of *p*-coumaric acid (hydroxylation on the aromatic ring or oxidative attack on the double bond of the lateral chain), and (v) the effect of dissolved oxygen on the removal of total organic carbon (TOC). These differences were interpreted in terms of reaction network of generation of radical oxygen species and of organics conversion. The possible formation of a surface peroxo adduct coordinated to a copper binuclear site was also evidenced for the solid heterogeneous catalyst.

**KEY WORDS:** copper; pillared clay; wet catalytic oxidation; WHPCO; H<sub>2</sub>O<sub>2</sub>; *p*-coumaric acid; TOF; H<sub>2</sub>O<sub>2</sub> efficiency; hydroxyl radical.

## 1. Introduction

The use of catalysts to improve the performances of water treatment technologies is known from several years, but only in the last decade more scientific attention was given to this aspect [1,2]. In fact, there is a need to improve current wastewater technologies for several reasons: (i) the increasing cost of wastewater treatment, (ii) the severe environmental regulations, (iii) an increasing attention to EPOC (Emerging Pollutant Categories of Concern, e.g. endocrine disrupting chemicals, hormonally active agents, xenobiotics, pharmaceutically active compounds, persistent organic pollutants etc.) and in general to effluent-derived microcontaminants and organic wastewater contaminants.

Wet hydrogen peroxide catalytic oxidation (WHPCO) is one of these advanced catalytic methods for the elimination of organic compounds in water [3]. The main advantages as compared to wet air (catalytic) oxidation (WACO) are that it avoids the use of costly reactors, can be selective towards the conversion of specific substrates and is easy to manage [3–6]. The only disadvantage it is that uses a more expensive reactant, although recent advances in the direct *in-situ* generation of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub>/O<sub>2</sub> [7,8] and reference therein] may open new perspectives to reduce H<sub>2</sub>O<sub>2</sub> cost.

H<sub>2</sub>O<sub>2</sub> is the precursor for generating hydroxyl radicals which are effective and highly active oxidizing species. This reaction occurs either using UV radiation or through the use of a catalyst (iron or copper ions) by the Fenton mechanism, where Fe<sup>2+</sup> or Cu<sup>+</sup> react with

H<sub>2</sub>O<sub>2</sub> to generate hydroxyl radicals. Due to the presence of a reaction cycle Fe<sup>3+</sup> and Cu<sup>2+</sup> ions could also be used (Fenton-like mechanism). However, there are two main side reactions which compete with this catalytic cycle: (i) the oxidation of the reduced transition metal ions by oxygen dissolved in water and (ii) the complexation of the transition metal ions by some of the intermediate oxidation reaction products, such as oxalic acid [9,10]. The use of solid Fenton-type catalysts instead of homogeneous salts in solution could limit these drawbacks, in addition to other advantages such as an easier recovery, a lower contamination of the effluents with metals which negatively influence the subsequent biological treatment step and a wider range of pH operations [9].

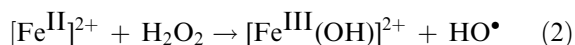
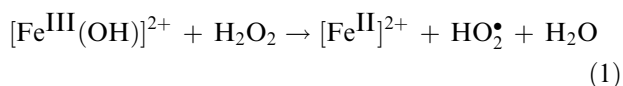
The development of solid Fenton-type catalysts has recently received significant attention. Transition metal exchanged zeolites [9–12], Cu<sup>2+</sup> containing montmorillonites [13,14] and Fe<sup>3+</sup> containing pillared clays [15] have been proposed as active catalysts for the oxidation of different organic compounds. These catalysts show a good rate of conversion of the pollutants and especially exhibit marginal leaching of the cations, keeping their activity almost same during successive runs [15]. Also other type of catalytic materials have been proposed [1,3], but the performances were generally lower or significant leaching was present.

The actual heterogeneity of the catalysis over Fenton-type catalysts in the H<sub>2</sub>O<sub>2</sub> solutions has often been a matter of discussion. Tatibouët *et al.* [15c] observed that both heterogeneous (Fe-pillared clays) and homogeneous (iron ions) Fenton-like catalysts show similar behaviour. However, heterogeneous catalysts are less sensitive to the pH and more efficient in total organic

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carbon (TOC) abatement. Kuznetsova *et al.* [16] showed that the contribution of homogeneous catalysis to the activity of FeZSM-5 in both the H<sub>2</sub>O<sub>2</sub> decomposition and C<sub>2</sub>H<sub>5</sub>OH oxidation does not exceed certain percents, even if leaching of iron was observed. In addition, they observed that in the presence of the iron ions complexing agents (P<sub>2</sub>O<sub>7</sub><sup>4-</sup> anions), FeZSM-5 showed a significantly different behaviour in comparison to the homogeneously dissolved iron cations. Catrinescu *et al.* [17] observed that in the phenol oxidation with H<sub>2</sub>O<sub>2</sub> over Fe-exchanged pillared beidellite the catalyst remains active even at neutral pH, while in homogeneous Fenton catalyst there is a very narrow range of activity around pH 3.0. In addition, they observed that Fe–Y zeolite show activity in pH conditions (above 5.0) where homogeneous iron ions are inactive, concluding that the reaction is heterogeneous. Guo and Al-Dahhan [18] studied the kinetics of WHPCO reaction of phenol over pillared clay Al-Fe catalyst instead concluded that the reaction takes place to a significant extent both in the liquid phase (homogeneous reaction) and on the catalyst surface (heterogeneous reaction). There are thus some discordances about the fact whether or not both homogeneous and heterogeneous reactions play a role on the performances of solid Fenton-like catalysts.

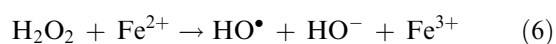
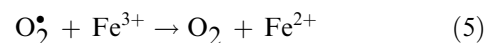
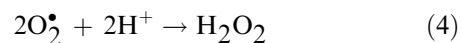
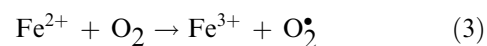
It is also unclear whether or not the solid Fenton-like catalysts give rise to some differences in the reaction mechanism, in terms of type of oxidizing species present in solution and/or pathways of degradation of the organic chemicals. Tatibouët *et al.* [15c], studying the oxidation of phenol with H<sub>2</sub>O<sub>2</sub> over Fe–Al pillared clays have determined the concentration of hydroxyl radicals by ESR DMPO (5,5-di-Me 1-pyrroline N-oxide) spin trapping experiments. HO• and HO<sub>2</sub>• were indicated as the more probable active species. They suggested the following reactions occurring in homogeneous or heterogeneous systems:



but also noted that the catalytic behaviour for the heterogeneous system appears to be slightly different to those observed for the homogeneous catalytic system. For the heterogeneous catalytic system, the reaction starts after an induction period (not observed for the homogeneous system) and the TOC abatement after 4 h of reaction is higher as compared to the homogeneous reaction. They suggested that both HO• and HO<sub>2</sub>• species participate in the reaction mechanism, but that the rate of radicals production is not enough to explain all the catalytic behaviour observed in the presence of the

solid catalyst. According to these authors this indicates that the difference between homogeneous and heterogeneous systems could either be due to the formation of different active oxygen species from hydrogen peroxide or to the ability of the heterogeneous catalyst to adsorb on the surface of phenol and/or the reaction intermediate products, favouring then their reaction with oxygen species formed by hydrogen peroxide activation.

Lloyd *et al.* [19] studying the origin of the hydroxyl radical in the Fenton homogeneous reaction reported that the trapped hydroxyl radical was derived exclusively from hydrogen peroxide and that no exchange of oxygen atoms between H<sub>2</sub>O<sub>2</sub> and solvent water occurs. More recent studies, however, present a different view of the reaction mechanism in the homogeneous Fenton reaction. Legube *et al.* [20] analyzing the behaviour of iron and copper homogeneous Fenton-like catalysts in the conversion of atrazine demonstrated that the mechanism is initiated by the formation of two Fe(III)-peroxo complexes at pH < 3.5 followed by their slow decomposition into Fe(II) and HO<sub>2</sub>•/O<sub>2</sub>•. Depending on the experimental conditions (nature and concentrations of the organic solutes, pH), the degradation of the organic compounds might be attributed to the hydroxyl radical or to other species like the cupryl ion [Cu(III)]. Production of Cu(III) by reaction of OH with Cu(II) has also been demonstrated by pulse radiolysis experiments. They also showed that for the Cu(II)/H<sub>2</sub>O<sub>2</sub> system, the decomposition of H<sub>2</sub>O<sub>2</sub> by Cu(II) goes through the formation of an intermediate (probably a Cu(II)-hydroperoxo complex). The rate of decomposition of H<sub>2</sub>O<sub>2</sub> by Cu(II) is affected by the concentration of dissolved oxygen, which is not true in the case of Fe(III) ions. Urbański and Berêsewicz [21] studied specifically the generation of HO• radicals initiated by interaction of Fe<sup>2+</sup> and Cu<sup>+</sup> with dioxygen in comparison with the Fenton mechanism (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>). They observed that metal autoxidation reaction may mediate HO• generation by this reaction sequence:



Furthermore, they noted that the process is enhanced by contaminating with Fe<sup>3+</sup> and Cu<sup>2+</sup> and/or the presence of reducing agents. Depending on the actual [H<sub>2</sub>O<sub>2</sub>]:[Fe<sup>2+</sup>] ratio, the efficiency of the Fe<sup>2+</sup>–O<sub>2</sub> chemistry to generate HO• was observed to be greater

than or, at best, equal to that of the  $\text{Fe}^{2+}$ -driven Fenton reaction.

Recently, new indication on the Fenton and Fenton-like chemistry in water have been provided from theoretical studies [22]. Alternative to the Haber and Weiss'  $\text{HO}\cdot$  radical mechanism (equation 3) [23], which has been usually indicated as the Fenton reaction, Baerends *et al.* [22] suggested an alternative mechanism (first proposed by Bray and Gorin [24]) in which the ferryl ion,  $[\text{Fe}^{\text{IV}}\text{O}]^{2+}$  is the active intermediate:

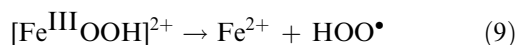


In both mechanisms, the hydrogen peroxide O–O lysis is the essential step. Static density functional theory (DFT) calculations of the active species produced by hydrated Fenton's reagent  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_5(\text{H}_2\text{O}_2)]^{2+}$  and *ab initio* molecular dynamics simulations of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  in aqueous solution indicate that (i) equation (7) is the predominant pathway with respect to equation (6) and (ii) ferryl ion formation from hydrated Fenton's reagent *in vacuo* is energetically favoured over the formation of free hydroxyl radicals. It is interesting to observe that the ferryl ion was suggested to be the actual species in the gas phase hydroxylation of benzene to phenol over FeMFI catalysts [25].

For the Fenton-like reagents, e.g. Fe(III) ion, initially no O–O bond breaking takes place, but instead an iron(III) hydroperoxo intermediate is formed as the first step *via* hydrolysis:



This intermediate might be able to react with organic substrates or break up in smaller active species in the second step. The iron(III) hydroperoxo may homolyze at the Fe–O bond generating iron(II) and producing the reactive  $\text{HOO}\cdot$  radical or at the O–O bond producing the ferryl ion and an  $\text{HO}\cdot$  radical:



Alternatively, O–O bond heterolysis could take place, producing the highly reactive  $\text{Fe}^{\text{V}}$  species:



Static DFT calculations on the hydrated Fenton-like reagent *in vacuo*,  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_5(\text{H}_2\text{O}_2)]^{3+}$ , and *ab initio* (DFT) molecular dynamics (AIMD) simulations of the Fenton-like reagent in aqueous solution,  $\text{Fe}^{3+}/\text{H}_2\text{O}_2(\text{aq})$  [22c] showed that the first reaction step consists of the donation of the  $\alpha$ -proton of hydrogen peroxide to the solvent shortly after the hydrogen peroxide coordinates to iron(III) (equation 8), and the second step involves probably the O–O bond homolysis

producing the ferryl ion and a hydroxyl radical (equation 10). A strong solvent effect was noted indicating that in the presence of ligands, particularly those inducing a low-spin iron(III) hydroperoxo intermediate, the pathway of transformation can be different.

This suggests that the anchoring of iron ions on an oxide surface may therefore induce a significant change in the pathway of transformation. The formation of the ferryl intermediate, e.g.  $[\text{Fe}^{\text{IV}}\text{O}]^{2+}$ , was also suggested to be a key step in the reaction mechanism over Fe-ZSM-5 Fenton-type solid catalysts [16], but they were suggested to form by oxidation of a Fe(III)-OH intermediate, not from the peroxo  $[\text{Fe}^{\text{III}}\text{OOH}]^{2+}$  species, and they were instead suggested to react with  $\text{H}_2\text{O}_2$  to generate  $\text{Fe}^{3+}$ ,  $\text{HO}_2^\bullet$  and  $\text{OH}^-$  species.

Therefore, Fenton and Fenton-like chemistry which is generally believed to proceed *via* similar mechanisms instead probably follows different reaction pathways, intermediates and reactive species. However, it is unknown whether or not this concept may be translated to solid Fenton-type catalysts. The presence of oxygen in solution may further influence this chemistry and it is unclear whether it may influence the Fenton or Fenton-like chemistry on solid catalysts. In addition, in a solid catalyst the organic reactant and/or the reaction intermediate products may adsorb on its surface favouring then their reaction with oxygen species formed by hydrogen peroxide activation.

In conclusions, there are many aspects for the comparison between homogeneous and heterogeneous Fenton catalysts which are unknown and a clarification of these aspects would lead to development of better catalysts for this important reaction. The aim of the work reported here is to contribute to a better understanding of these issues by comparing the performances of copper Fenton-like homogeneous and heterogeneous catalysts. In particular, a copper-pillared clay (Cu-PILC) was used as solid Fenton catalyst, because this catalyst does not show copper leaching as compared to other copper-based solid Fenton catalysts [26] and in general copper-based Fenton catalysts have been studied less in detail than iron-based Fenton catalysts. As model compound for the investigation *p*-coumaric acid was used, because this compound has been often used in literature as representative of biorecalcitrant phenolic compounds found in the olive oil processing waste water [1].

## 2. Experimental

### 2.1. Preparation of the catalysts

The Cu-PILC catalyst has been prepared by pillaring procedure of a clay (commercial bentonite from Sigma-Aldrich), using a diluted aqueous solution of NaOH containing  $\text{Al}^{3+}/\text{Cu}^{2+}$  ions [14]. The cationic solution containing 0.18 and 0.02 mol/L of  $\text{AlCl}_3$  and  $\text{CuCl}_2$ , respectively, was prepared by slow addition of a 0.2 M

NaOH solution to the solution containing the metal salt up to arrive to an OH/metal ratio of about 2 under constant stirring (temperature of 70 °C). Then the intercalating solution was added very slowly at room temperature to the previously prepared aqueous suspension of the clay (2% by wt.). The final ratio (Al + Cu)/clay was 3.8 mol/Kg. After ageing for 20 h in the presence of the mother liquor, the solid is recovered by filtration. It is then washed for a long time with distilled water till complete elimination of Cl<sup>-</sup> ions from the washing solution. The solid is then dried at 70 °C and calcined at 500 °C for 2 h (2 °C/min). The content of copper in the above prepared catalysts was 2.0% and the surface area 107 m<sup>2</sup>/g. The preparation was well reproducible.

This sample will be indicated as Cu(2)PILC herein after. The Cu(1)PILC and Cu(0.5)PILC samples were prepared, containing 1% and 0.5% wt. Cu, respectively by following the above procedure.

### 2.2. Characterization

The chemical analysis of the samples was made by X-ray fluorescence (XRF) method (Minipal, Philips), while the amount of leached metals was determined using a Perkin-Elmer 400 atomic adsorption spectrophotometer on the solution after hot-filtration (at the same temperature of the reaction) of the solution.

The BET surface area were measured using nitrogen sorption at 77 K. Prior to the experiments, the samples were outgassed at 100 °C for 5 h. The isotherms were measured using a Micrometrics ASAP 2010 system.

UV-visible diffuse reflectance (UV-VIS-DR) spectra were recorded in air on powdered samples using a Jasco V-570 spectrometer equipped with an integrating sphere for solid samples. The reference was BaSO<sub>4</sub>.

### 2.3. Reactivity tests

*p*-Coumaric acids oxidation was carried in the semi-batch mode using a stirred and thermostated pyrex slurry reactor of 250 mL. Hundred mL of an aqueous *p*-coumaric acid solution (500 mg/L) was heated to 70 °C or 80 °C; after the stabilization of the temperature, the solid catalyst (0.5 g) or the copper ions (as Cu<sup>2+</sup>-nitrate, in an amount in the 6–68 μmoles range which corresponds roughly to the amount of copper present in 0.5 g of the solid catalyst) was introduced. After estimating the initial concentration of the solution, the continuous feed of the H<sub>2</sub>O<sub>2</sub> (concentration 35% wt.) at a rate of 0.3 or 0.5 mL/h was started and monitored periodically to find the presence of adsorption on the catalyst. Reaction tests were made at the natural pH.

The conversion of the reactant (*p*-coumaric acid) and the formation of the products of reaction was analysed by a High performance liquid chromatograph (Dionex HPLC) equipped with a C18 column (Omnispherb C18 Varia, 250×4.6 mm). The TOC of the solution was

determined with a TOC analyzer model 5000 A (Shimadzu). The analysis of the residual H<sub>2</sub>O<sub>2</sub> in solution was made by iodimetric titration using an automatic electrochemical apparatus (Titrino, Metrohm).

Preliminary tests were made to check the reactivity of H<sub>2</sub>O<sub>2</sub> without the presence of the catalyst, and the evaluation of the contribution of adsorption phenomena on the catalyst.

## 3. Results and discussion

### 3.1. Comparison of the performances of homogeneous and heterogeneous catalysts

Compared in figure 1A are the conversion of *p*-coumaric acid versus the time of reaction for homogeneous Cu<sup>2+</sup> ions (three levels of copper ion concentration) and for heterogeneous CuPILC catalysts (three samples at increasing copper loading). A fast conversion of *p*-coumaric acid is noted in all samples. A complete *p*-coumaric acid conversion is reached in 1 h of reaction or less, except for the homogeneous catalyst having the lowest copper concentration. The activity increases with

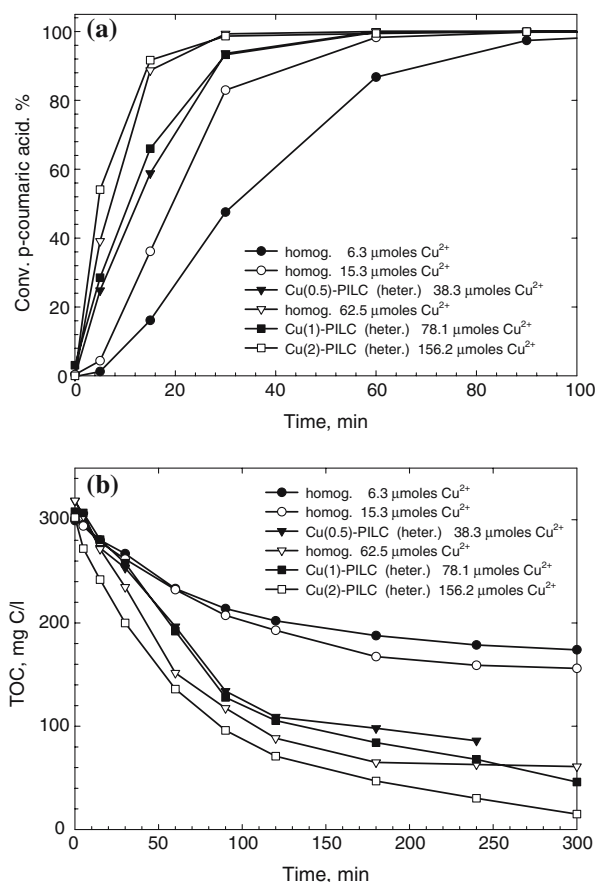


Figure 1. Conversion of *p*-coumaric acid (a) and total organic carbon (TOC) variation (b) as a function of the time of reaction for homogeneous (copper-nitrate) and heterogeneous (CuPILC) catalysts. Reaction conditions: 80 °C, rate of H<sub>2</sub>O<sub>2</sub> addition of 0.3 mL/h.

the increase in concentration of copper in solution (homogeneous catalyst) or on the solid catalyst. For a similar copper amount, homogeneous and heterogeneous Fenton-like catalysts have a similar behaviour.

For the two tests with the homogeneous catalysts and a concentration of copper of 6 or 15  $\mu\text{moles}$ , the presence of an induction time (about 5 min) was observed. No leaching of copper was observed after the tests with the CuPILC samples, at least above the detection limit of about 1 ppm.

Reported in figure 1B are the curves of the variation of the TOC versus the time of reaction for the same catalysts of figure 1A. In general the TOC abatement also increases with the increase in concentration of copper and a similar behaviour between the homogeneous and heterogeneous catalysts is observed. However, for the homogeneous catalyst after about 3 h of reaction, the TOC value reaches a nearly constant behaviour, while CuPILC catalysts still continue to be active towards the abatement of the TOC. This effect can be explained as due to the complexing effect of the products of reaction (oxalic acid, in particular) towards copper ions which inhibits their activity as Fenton-like catalysts, as explained in case of iron Fenton-like catalysts [1].

### 3.2. Turnover frequency (TOF)

Figure 2 analyzes the data reported in figure 1 in terms of TOF per copper ion, assuming all copper ions are active in the reaction. Figure 2A reports the TOF estimated with respect to the conversion of *p*-coumaric acid, while figure 2B shows the TOF with respect to TOC abatement:

$$\text{TOF}_{\text{pCA}} = \frac{\text{moles } (p\text{-coumaric acid converted})}{\text{moles Cu}^{2+} \cdot \text{h}}$$

$$\text{TOF}_{\text{TOC}} = \frac{\text{moles (moles C mineralized)}}{9 \cdot \text{moles Cu}^{2+} \cdot \text{h}}$$

Considering that each molecule of *p*-coumaric acid contains 9 carbon atoms, it was necessary to normalize the TOF estimated for TOC abatement by dividing it by nine. The TOF refers to the initial activity, e.g. extrapolated at zero time. However, the two tests with the homogeneous catalysts and a concentration of copper of 6 or 15  $\mu\text{moles}$ , show the presence of an induction time. Therefore, figure 2A reports for these two samples both the initial TOF and that estimated after the induction time, e.g. after about 5 min. The value obtained are comparable with those reported by Kiwi *et al.* [27] for the photo-Fenton degradation of Orange II, taking into account the differences in the two systems.

The  $\text{TOF}_{\text{pCA}}$  (figure 2A) and  $\text{TOF}_{\text{TOC}}$  (figure 2B) decreases on increasing the copper concentration, at least if we consider the data after the induction time for the homogeneous case. The first possible interpretation of this trend could be as follows: the rate of generation

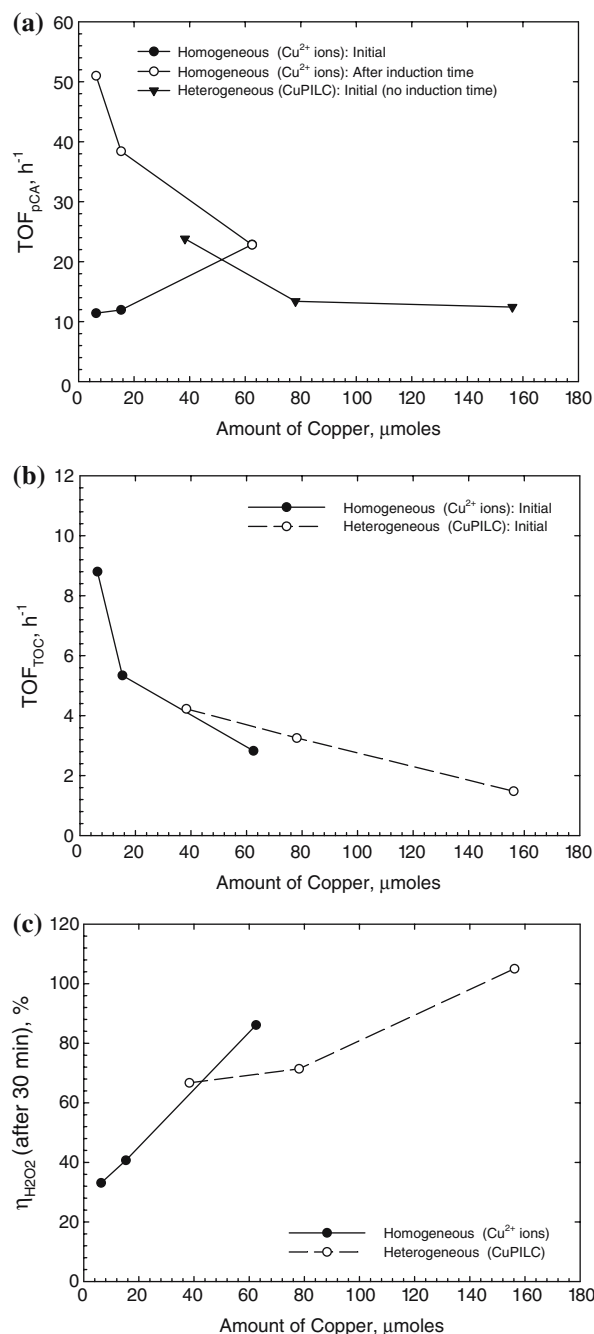


Figure 2. Turnover frequency (TOF) in *p*-coumaric acid conversion (a) and in TOC removal (b), and efficiency in the use of H<sub>2</sub>O<sub>2</sub> after 30 min of reaction (c) as a function of the total amount of copper in solution (homogeneous case) or on the solid catalyst (heterogeneous case). Reaction conditions as in figure 1.

of the radical active species (HO<sup>•</sup>, HOO<sup>•</sup>) depends linearly on the concentration of copper, while the rate of their recombination (termination) shows a higher reaction order. Therefore, a decrease of the turnover could be expected on increasing the copper concentration.

According to this interpretation, it may be expected that the efficiency in the use of H<sub>2</sub>O<sub>2</sub> decreases on increasing the copper concentration, because the rate of termination of the HO<sup>•</sup> and HOO<sup>•</sup> radical species

increases. Figure 2C reports the efficiency in use of  $\text{H}_2\text{O}_2$  (after 30 min of reaction) as a function of the amount of copper ions in the homogeneous and heterogeneous catalysts. It should be noted that these tests have been made in a semi-batch well-mixed reactor using a constant rate of  $\text{H}_2\text{O}_2$  addition during the reaction.

Considering that the following reaction leads to the mineralization of the *p*-coumaric acid, e.g. to the reduction of the TOC:



and considering that the rate of  $\text{H}_2\text{O}_2$  addition in the tests reported in figure 1B was 0.3 mL/h, it is possible to calculate the theoretical TOC reduction ( $\Delta\text{TOC}_{\text{th}}$ ) expected if all the added  $\text{H}_2\text{O}_2$  is consumed to convert the *p*-coumaric acid according to equation (12). The ratio between the experimental variation of the TOC ( $\Delta\text{TOC}_{\text{exp}}$ ) and the theoretical TOC reduction gives the efficiency ( $\eta$ ) in the use of  $\text{H}_2\text{O}_2$ :

$$\eta_{\text{H}_2\text{O}_2}(\%) = 100 \cdot \frac{\Delta\text{TOC}_{\text{exp}}}{\Delta\text{TOC}_{\text{th}}} \quad (13)$$

It should be noted that values higher than 100% are possible, when the dissolved oxygen participates in the reaction mechanism (see later). On increasing the copper amount there is an increase in the efficiency of  $\text{H}_2\text{O}_2$  use, both in the homogeneous and heterogeneous cases (figure 2). This indicates that the above interpretation of the decrease in the TOF with the increase in the amount of copper (figure 2A and 2B) is not valid, at least in the investigated experimental range.

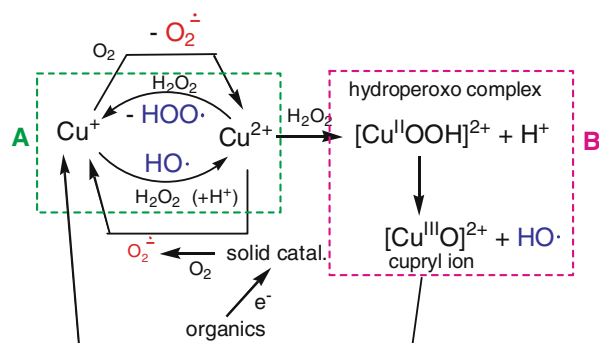
For the heterogeneous case it may be possible that not all copper ions are accessible or active in the Fenton reaction and that decreasing the copper dispersion, e.g. increasing the copper loading in CuPILC samples, increases the relative fraction of these less active copper species. A decrease in the TOF could be thus expected. However, this interpretation cannot be used for the homogeneous case, if we are not assuming the formation of different copper complexes by increasing the copper concentration. However, there are no data in literature which support this explanation. In addition, above interpretation cannot explain why the efficiency of  $\text{H}_2\text{O}_2$  increases on increasing the copper loading (figure 2C). Therefore, a different interpretation is necessary.

It may be noted that an induction time is necessary for the homogeneous catalysts. This induction time could be reasonably attributed to the partial reduction of  $\text{Cu}^{2+}$  ions to  $\text{Cu}^+$  ions for example by the organic species present in solution, but which occurs only when  $\text{H}_2\text{O}_2$  is added. This reduction introduces more efficient copper species in the generation of oxygen radical species explaining the about four-fold increase in the TOF after the induction period (figure 2A). It is reasonable to analyze the possible link between this effect of induction time and the observed trend in TOF with respect to

copper concentration. Prior to proposing this possible relationship, it is necessary to discuss before the reaction pathways leading to the generation of the radical oxygen species responsible for organics degradation.

### 3.3. Reaction pathways in the generation of the radical oxygen species

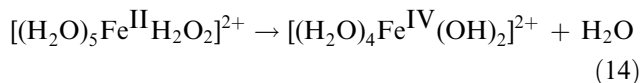
Scheme 1 shows an overview of the possible reaction pathways in the Fenton and Fenton-like mechanisms (see introduction). Besides the “classic” redox cyclic mechanism involving  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  species (indicated with A in scheme 1), an additional pathway with formation of a copper hydroperoxo complex intermediate which transforms then to cupryl ion generating an hydroxyl radical is possible (indicated with B in scheme 1). The mechanism is based on the hypothesis proposed for Fenton-like iron catalysts and may be valid also for copper as well. It is reasonable to assume that the two pathways are characterized by different turnover frequency as well as efficiency in  $\text{H}_2\text{O}_2$  use. In our case, starting from  $\text{Cu}^{2+}$  ions (Fenton-like catalysts), the presence of the pathway A or B depends on the energetic stability of the hydroperoxo complex (see introduction), which in turns depends on the ligand effect of the substituents. As far as we know, there are no theoretical studies in literature about the species which forms by interaction of  $\text{H}_2\text{O}_2$  with  $\text{Cu}^{2+}$  ions, but let us assume it is similar to what proposed for  $\text{Fe}^{3+}$  ions [22], the preferable pathway involves the formation of the  $\text{Cu}^{2+}$  hydroperoxo complex (pathway B in scheme 1). Further transformation give rise to the formation of hydroxyl radicals and cupryl ions. The latter may oxidize organic molecule thereby reducing to  $\text{Cu}^+$  ions. As noted for  $\text{Fe}^{3+}$  ions [22], the change from aquo to organic ligands in the copper complex may change the stability of the hydroperoxo complex. It is therefore reasonable to suggest that in the homogeneous catalyst the initial Fenton mechanism involves the hydroperoxo complex (route B), while in the progress of the reaction the mechanism changes to the “ $\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+}$ ” cyclic one (route A) as a consequence of the change in the



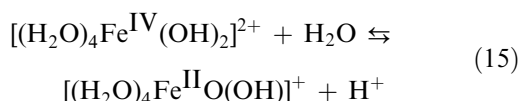
Scheme 1. Reaction mechanism in the generation of radical oxygen species by interaction with  $\text{H}_2\text{O}_2$  with copper ions in solution or on the solid catalyst.

formation of products of reactions (oxalic acid, for example) which substitute water molecules in coordinating the copper ions. This explains the presence of an induction time and the related change in the turnover frequency.

Recent theoretical studies [22,28] have shown that the Fe(II)-aquo complex dissociates fast after coordination of H<sub>2</sub>O<sub>2</sub> to a hydroxo group coordinated to iron and an HO• radical which attacks a solvent water molecule that was hydrogen bonded to the hydrogen peroxide. In fact, the generated hydroxyl radical has a short life time which restrict its effective range of action to a few nanometers. When the organic substrate concentration is high there is a good chance that the hydroxyl radical may react with the organic molecule in the neighbourhood of the iron complex where the hydrogen peroxide is coordinated. Therefore, the HO• radical contributes to the oxidation reactions, because the radical transfer could find a path along an H-bond attached to an organic substrate molecule if the latter is close enough. Otherwise, the radical passage can go *via* a few solvent water molecules and end up with hydrogen abstraction from one of the water ligands of the same iron complex, resulting in the formation of a dihydroxo complex:



The iron(IV)dihydroxo complex is in equilibrium with its conjugate base:



After few pico-seconds, one of the water ligands leaves the first solvation shell, but the formed complex  $[(\text{H}_2\text{O})_3\text{Fe}^{\text{IV}}\text{O}(\text{OH})]^{+}$  undergoes no more spontaneous chemical changes in the next pico-seconds [28].

In other words, if the hydroxyl radical formed by the Fe<sup>II</sup> aquo-complex and H<sub>2</sub>O<sub>2</sub> does not encounter an organic molecule in the neighbourhood, the process leads to a quenching of the hydroxyl radical. However, if the pentaqua iron(II) hydrogen peroxide complex would be in the neighbourhood of a hexaaqua iron(II) complex, the HO• radical passage might be, *via* two or three solvent water molecules, to a water ligand of the hexaaqua iron(II), with two mono-hydroxo pentaqua iron(III) complexes as the result. Their further transformation generate new radical species. For higher iron concentrations, there is thus an additional pathway of reaction of the short-lived hydroxyl radicals. Recent studies by laser light scattering [29] have shown that the effective diameter of Fe(II) action in the Fenton reaction increases on increasing the iron concentration. This agrees with what was discussed above, because the hydroxyl radical reaction with a neighbouring iron complex extend its area of action. Therefore increases the probability that the

hydroxyl radical reacts with an organic molecule and the efficiency of the use of H<sub>2</sub>O<sub>2</sub>. It is known, on the other hand, that optimal iron/H<sub>2</sub>O<sub>2</sub> and iron/organics ratios exist to maximize the Fenton and Fenton-like processes, in agreement with the above mechanistic interpretation.

As far as we know there are no similar studies for copper Fenton and Fenton-like catalysts, but it is reasonable to suggest the presence of similar mechanisms. This explains why increasing the copper concentration a reduction of the TOF is observed together with an increase in the efficiency in H<sub>2</sub>O<sub>2</sub> use. In fact, increasing copper concentration decreases the H<sub>2</sub>O<sub>2</sub>/Cu<sup>2+</sup> ratio, but increases the probability to have two neighbouring copper complex and thus the possibility of limiting the quenching of the generated hydroxyl radicals.

In the solid catalyst (CuPILC) a similar trend is observed, e.g. a decrease in the TOF and an increase in the H<sub>2</sub>O<sub>2</sub> efficiency on increasing the copper loading. Reasonably the same interpretation is valid for the heterogeneous system also. However, no induction time was observed for the solid catalysts, indicating that the interaction of the ligand effect of the oxide substrate to the copper ions probably inhibits the pathway B in scheme 1.

### 3.4. Byproducts formation

The distribution of the byproducts in *p*-coumaric acid conversion over Cu(2)PILC and Cu<sup>2+</sup> homogeneous catalyst (62 mmols Cu<sup>2+</sup>) is shown in figure 3A and 3B, respectively. Oxalic acid is the main byproduct in both cases, although, after about 4 h of reaction, its formation is about two times higher in case of heterogeneous catalyst (CuPILC). The other byproducts and their amount is almost similar for the homogeneous and heterogeneous systems.

A closer inspection of the nature of byproducts allows to outline the reaction network of *p*-coumaric acid degradation schematically reported in scheme 2. There are two main pathways for the conversion of *p*-coumaric acid: (i) hydroxylation of the aromatic ring resulting in the formation of caffeic acid (CA) and (ii) epoxidation of the double bond of the lateral chain with the intermediate formation of the corresponding diol which is then quickly converted to 4-hydroxybenzaldehyde (4HB) with the elimination of oxalic acid. There are various possible pathways of subsequent degradation. Scheme 2 reports a pathway which appears probable. The possibility of other pathways cannot be ruled out.

After caffeic acid formation it is possible to have the attack on the double bond in the lateral chain to form the 3,4 dihydroxybenzaldehyde which can also be formed by hydroxylation of the aromatic ring of 4HB. Oxidation of the 3,4 dihydroxybenzaldehyde gives 3,4 dihydroxybenzoic acid and further conversion of this compound gives a sequence of intermediate products

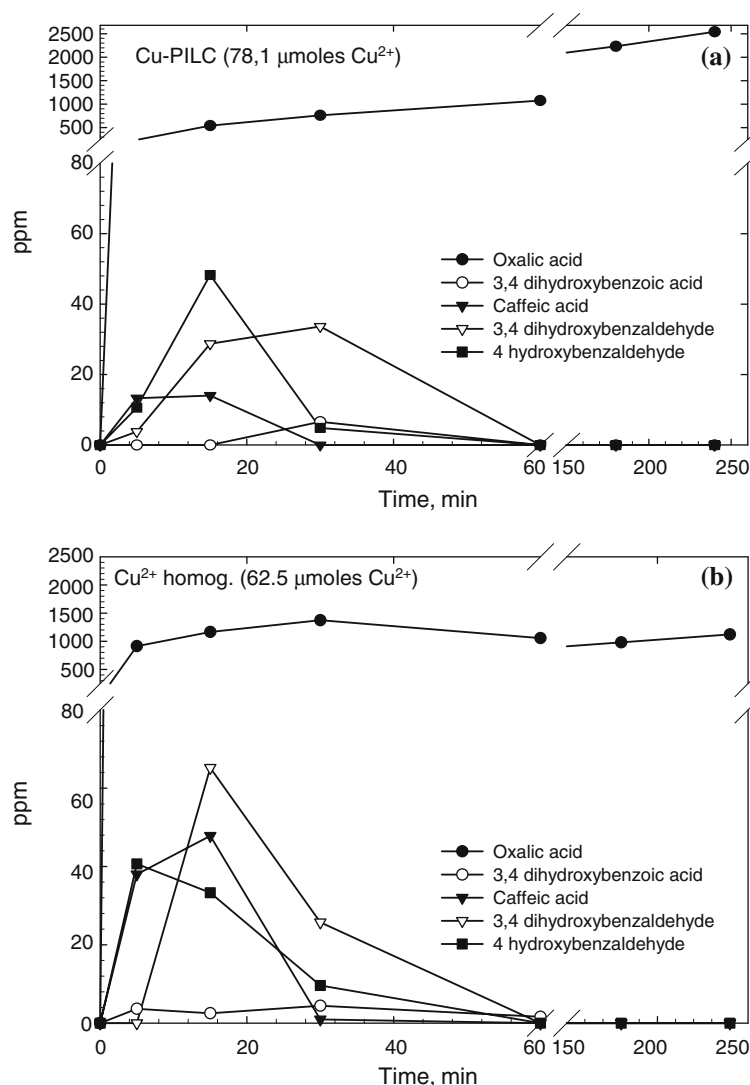


Figure 3. Formation of byproducts as a function of the time of reaction for heterogeneous catalyst [Cu(1)PILC] (A) and homogeneous catalyst (62,5 μmoles of Cu<sup>2+</sup> ions in solution) (B). Reaction conditions as in figure 1.

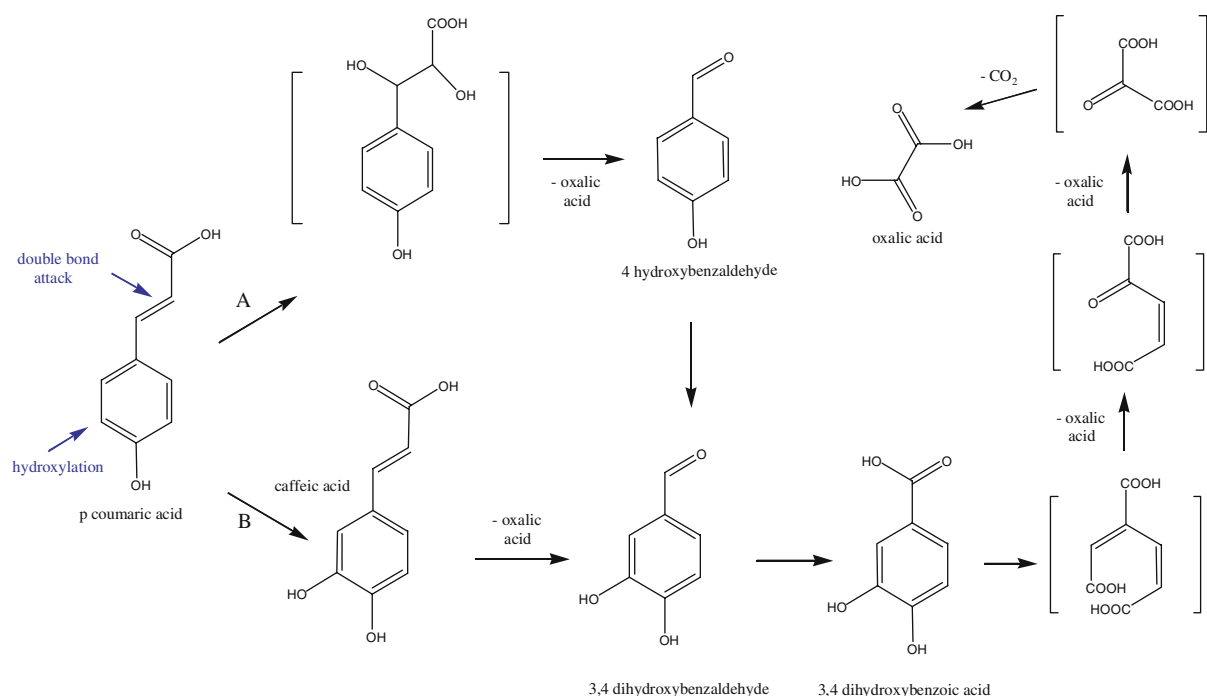
such as triacids etc., which are difficult to identify analytically. Finally the degradation of these intermediates gives oxalic acid as stable product recalcitrant to further conversion and transformation to CO<sub>2</sub>.

According to this reaction scheme, two different oxidizing attacks are possible on the *p*-coumaric acid, the epoxidation on the double bond of the lateral chain which forms 4HB as first identified product and the hydroxylation of the aromatic ring which gives CA. Therefore, it is interesting to analyze the formation of these products in the homogeneous and heterogeneous cases and how the ratio of these two products changes as a function of time. Figure 4 overviews these results. There is a different trend with respect to the time on stream of the CA/4HB ratio for the homogeneous and heterogeneous cases. In the latter CA is mainly formed almost immediately, while in the homogeneous case the CA takes some time (around 15 min) to reach its maximum formation. This suggests an evolution in the

nature of the active sites in the homogeneous case which agree with the previous discussion about the mechanism responsible for an induction time in *p*-coumaric acid conversion.

It may be tentatively suggested that the attack on the double bond of the lateral chain first followed by the hydroxylation of the aromatic ring (pathway A in scheme 2) is due to the route involving the hydroperoxo complex formation, while the pathway B (first hydroxylation of the aromatic ring and then attack on the lateral chain) involves the “Cu<sup>+</sup> ⇌ Cu<sup>2+</sup>” cyclic mechanism. The first mechanism (*via* hydroperoxo complex) initially dominates the conversion in the homogeneous case, but then a progressive change to the “Cu<sup>+</sup> ⇌ Cu<sup>2+</sup>” cyclic mechanism, is achieved as discussed before. This explains the initial increase in the CA/4HB ratio in the homogeneous case after the induction time (figure 4). The ligand effect of the oxide in the case of the CuPILC instead, inhibits the





Scheme 2. Reaction mechanism in the conversion of *p*-coumaric acid. The compounds in the bracket were supposed as reaction intermediate, but not identified analytically.

pathway *via* the hydroperoxo complex. Therefore, the “ $\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+}$ ” cyclic mechanism is already the dominant route and CA/4HB ratio is already high at the beginning. The ratio then decreases due to the conversion of the caffeic acid itself.

Therefore, the analysis of the trends in byproducts formation with the time of reaction for the homogeneous and heterogeneous catalysts, further support the discussion in the previous section regarding the reaction pathways in the generation of the radical oxygen species.

### 3.5. Effect of $\text{O}_2$

As indicated in the introduction and outlined also in scheme 1, dissolved oxygen in solution may also play a role in the mechanism of generation and/or quenching of radical oxygen species. Therefore, it is interesting to understand whether this effect is present and if differences between the homogeneous and heterogeneous cases could be evidenced.

Reported in figure 5A is the conversion of *p*-coumaric acid and the variation of TOC as a function of the time of reaction for  $\text{Cu}(2)\text{PILC}$  catalysts during tests in air as in the previous tests or when, instead, a flow of  $\text{N}_2$  was bubbled to the solution to reduce the amount of the dissolved  $\text{O}_2$ . A minimal effect on the conversion of *p*-coumaric acid and a significant effect is observed on the removal of TOC.

Figure 5B shows the comparison of the effect of a  $\text{N}_2$  flow bubbled to eliminate the dissolved  $\text{O}_2$  on the TOC after 1 h of reaction for the homogeneous and heterogeneous cases. There are two opposite effects of  $\text{O}_2$ . In

the heterogeneous case, the presence of  $\text{O}_2$  promotes the reaction, e.g. allows to reduce the TOC after 1 h. In the case of the homogeneous system, the presence of oxygen instead lowers the reactivity.

Oxygen dissolved in solution may give rise to the conversion of  $\text{Cu}^+$  species to  $\text{Cu}^{2+}$  forming  $\text{O}_2^{\bullet-}$  (scheme 1), reducing therefore the efficiency of the “ $\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+}$ ” cyclic pathway (route A). Therefore, it is reasonable that for the homogeneous catalysts, fluxing the solution with  $\text{N}_2$  to reduce the amount of dissolved  $\text{O}_2$  improves the level of TOC reduction. In the heterogeneous case, however,  $\text{O}_2^{\bullet-}$  species may be generated from the chemisorption of dissolved oxygen on the catalyst and the reaction with electrons generated from the conversion of the organic species on the catalyst surface. These  $\text{O}_2^{\bullet-}$  may react with  $\text{Cu}^{2+}$  species forming  $\text{Cu}^+$  species (scheme 1) introducing a further pathway for generation of  $\text{Cu}^+$  species. In other words the dissolved oxygen mediates the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  by electrons produced in the conversion of organics over the catalyst surface. This is reasonable considering the relatively poor solid electron transfer characteristics of  $\text{CuPILC}$ . In addition, dissolved oxygen and/or the species generated by oxygen chemisorption on the catalyst may also participate in the mechanism of oxidation of the organic species. The result of these two effects leads to a promotion of oxygen of the TOC reduction in the case of the heterogeneous catalyst, while the opposite effect is present in the case of the homogeneous catalyst. It should be noted that in the case of heterogeneous catalysis, the participation of dissolved oxygen in the reaction mechanism and its resulting

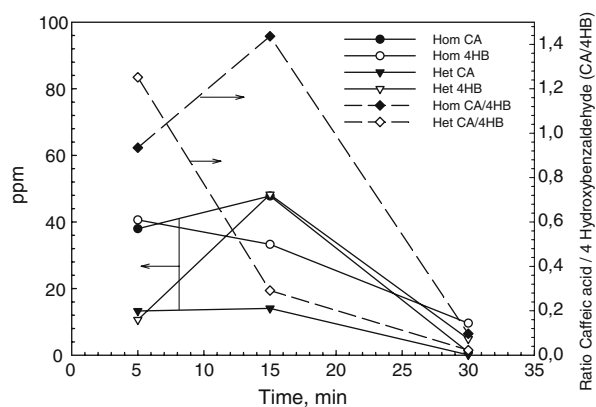


Figure 4. Formation of byproducts and change of the ratio between caffeic acid (CA) and 4-hydroxybenzaldehyde (4HB) as a function of the time of reaction for heterogeneous catalyst [Cu(1)PILC] (a) and homogeneous catalyst (62,5  $\mu\text{moles}$  of  $\text{Cu}^{2+}$  ions in solution) (b). Reaction conditions as in figure 1.

promotion effect explains the higher than 100% efficiency in the use of  $\text{H}_2\text{O}_2$  for the Cu(2)PILC catalyst (figure 2C).

The effect of the deoxygenation of the solution on the product distribution for Cu(2)PILC catalyst is shown in figure 6A and 6B (tests in air and in flux of  $\text{N}_2$ , respectively). Figure 6C reports instead the conversion of caffeic acid to 4 hydroxybenzaldehyde (CA/4HB) as a function of the time of reaction for the tests in air and bubbling  $\text{N}_2$ . No remarkable change in the distribution of the products is observed for the two experiments. However, for the deoxygenated solution an increase in the relative formation of caffeic acid is observed. This fact is in agreement with the previous discussion indicating a promotion effect of dissolved oxygen in the generation of  $\text{Cu}^+$  species. The similar distribution of the products of reaction instead indicates a minor role of dissolved oxygen as a direct oxidizing agent, although no conclusive evidences are present about this aspect.

### 3.6. Chemisorption of the organic species on the solid catalyst

In the heterogeneous catalyst the chemisorption of the organic molecule on the catalyst surface leads to a higher concentration of organic species near to the active sites. An increase of the probability that the short living radical species oxidize the organics instead to be quenched through the mechanisms discussed above is expected. It is therefore interesting to analyze if there is a chemisorption of organic species during the catalytic reaction occurs and if these chemisorbed organic species react during the reaction.

To analyze these aspects, the change of the UV-visible diffuse reflectance spectrum of the Cu(2)PILC catalyst after different times of reaction (figure 7) was monitored. The samples after catalytic reaction were dried before the analysis.

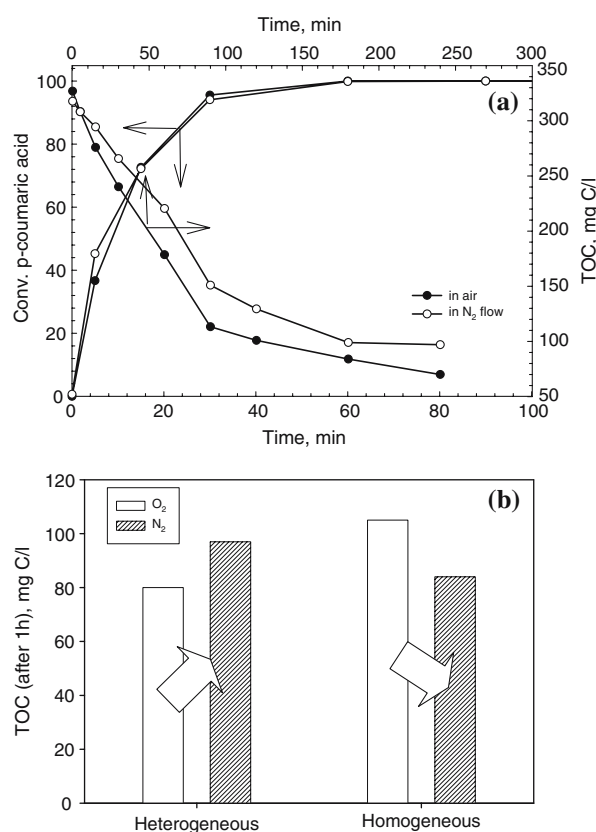


Figure 5. (a) Comparison of the conversion of *p*-coumaric acid and TOC variation as a function of the time of reaction for Cu(2)PILC heterogeneous catalysts: tests in air or under flux of  $\text{N}_2$  to remove adsorbed oxygen. (b) TOC after 1 h for the heterogeneous catalyst [Cu(2)PILC] and homogeneous catalyst (62,5  $\mu\text{moles}$  of  $\text{Cu}^{2+}$  ions in solution) in tests in air or under flux of  $\text{N}_2$  to remove adsorbed oxygen. Reaction conditions: 70 °C, rate of  $\text{H}_2\text{O}_2$  addition of 0.3 mL/h.

The fresh catalyst (spectrum 1) shows a main intense band near 260 nm and a very broad tail extending up to about 800 nm where not well-resolved shoulders centred at about 340 nm and 500 nm could be identified. The main band at 260 nm could be assigned to the charge-transfer oxygen to  $\text{Cu}^{2+}$  band of the ions present in the octahedral layer of the clay mineral similarly to what observed for  $\text{Zr}^{4+}$  or  $\text{Fe}^{3+}$  ions in pillared clays [30,31]. The two shoulders at lower frequencies could be attributed to the charge-transfer (ligand to metal) in copper oxide clusters (in distorted square-pyramidal coordination) and in chain-like structures, respectively [31], localized in the clay pillars.

After 30 min of reaction two new components growth at about 325 nm and 575 nm. A general increase in the intensity of the long tail was observed. These bands disappear after about 4 h of reaction and the spectrum returns coincident with that of the original fresh sample. After 4 h, only residual oxalic acid is detected in solution (about 2000 ppm, figure 3A). This indicates that the new bands observed after 30 min of reaction cannot be attributed to the chemisorption of the main product

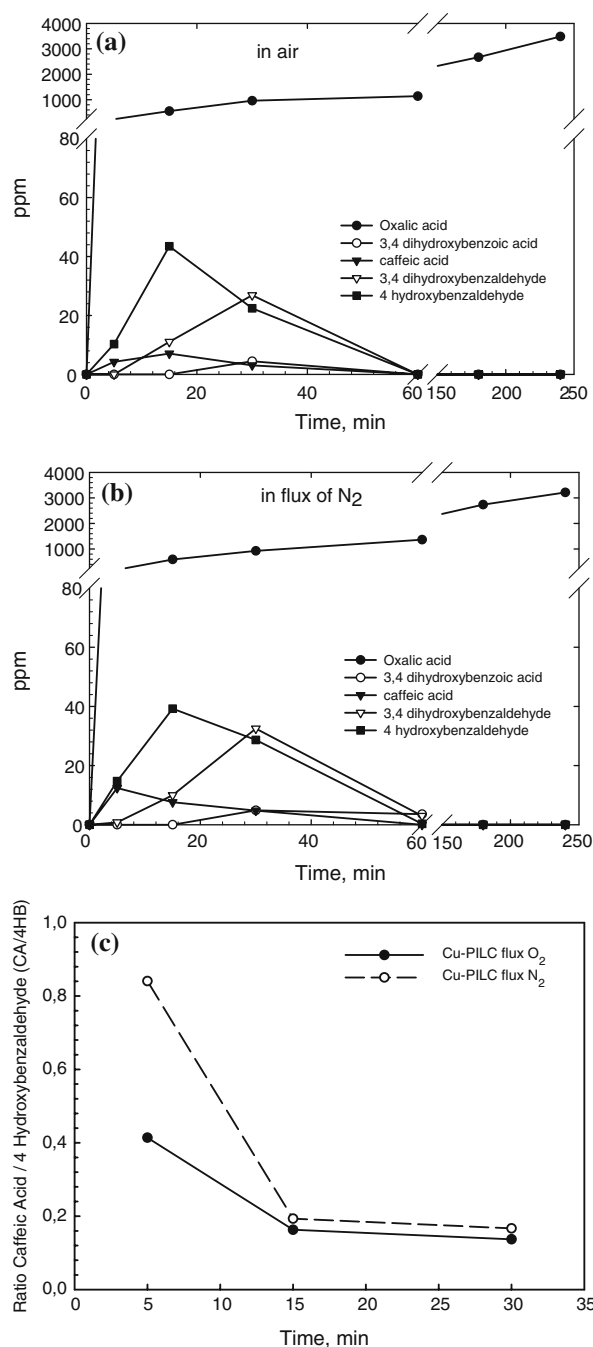


Figure 6. Byproducts as a function of the time of reaction for Cu(2)PILC heterogeneous catalysts: tests in air (a) or under flux of N<sub>2</sub> (b). (c) Comparison of the ratio between caffeic acid (CA) and 4-hydroxybenzaldehyde (4HB) as a function of the time of reaction for Cu(2)PILC and tests in air or flux of N<sub>2</sub>. Reaction conditions as in figure 5.

of reaction, which is oxalic acid, because otherwise these bands should also be observed in the spectrum after 240 min.

*p*-Coumaric acid shows an adsorption maximum near 320 nm, but after 30 min it is completely converted during the catalytic tests with Cu(2)PILC (figure 1A). Coumarins and similar carboxylic acids may form

binuclear complexes of copper(II) characterized by an oxygen to metal charge-transfer band near 385 nm and a band in the visible region (near 700 nm) attributed to d–d transitions with enhanced intensity [32,33], because they become spin-allowed due to the specific complex configuration. It is thus possible, in principle, that the bands observed at 325 and 575 nm (after 30 min of reaction) may be due to the formation of a surface complex between carboxylic acids formed during *p*-coumaric acid conversion and copper surface dimers. However, an alternative and more reasonable interpretation in our opinion, derives from the observation that enzymes characterized by an oxy-hemocyanin structure such as the *horseshoe crab* (the structure is outlined in scheme 3 show intense bands at 345 and 570 nm, assigned both to oxygen to Cu<sup>2+</sup> charge-transfer transitions [34].

The bands at 325 and 575 nm observed after 30 min of reaction may be attributed to the formation of an analogous complex on the surface of CuPILC and, its formation may be possibly increased by the chemisorption of the reaction intermediates on the catalyst. These bands, in fact, are not seen by contacting H<sub>2</sub>O<sub>2</sub> with the CuPILC catalyst, or on the catalyst after 4 h of reaction (figure 7), where oxalic acid along with some unconverted H<sub>2</sub>O<sub>2</sub> is present in the solution.

It is not possible to conclude from the present data if the species indicated in scheme 3 may play a role in the Fenton-type oxidation mechanism of these catalysts. The data indicate that the active copper species present may be different in case of homogeneous and heterogeneous Fenton-like catalysts in spite of similar catalytic performances.

Finally, the fact that after reaction the UV-Visible spectrum of Cu(2)PILC is the same as that of the fresh one (figure 7) further supports the indication of the

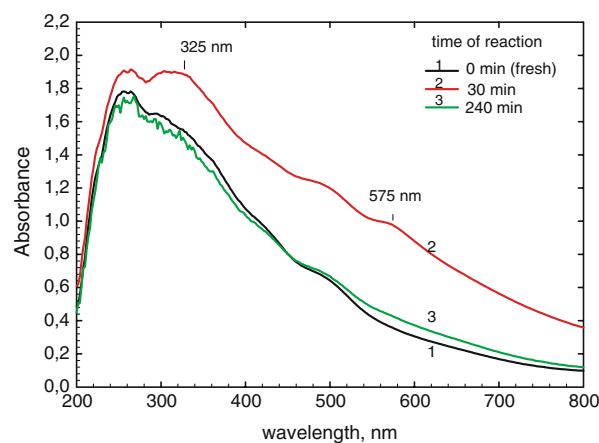
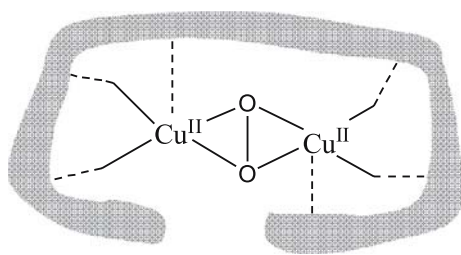


Figure 7. UV-Visible diffuse reflectance spectra of fresh Cu(2)PILC (spectrum 1), and after 30 min and 240 min of reaction in WHPCO of *p*-coumaric acid (spectra 2 and 3, respectively). Reaction conditions as in figure 1. The sample after reaction were dried at 120 °C before to record the diffuse reflectance spectra.



Scheme 3. Model of coordination of oxygen in the enzyme *horseshoe crab*. Elaborated from ref. [34].

stability of these heterogeneous catalysts and their possible use also in continuous operations.

#### 4. Conclusions

The comparison between homogeneous ( $\text{Cu}^{2+}$  ions) and heterogeneous ( $\text{Cu}^{2+}$ -pillared clay) Fenton-like catalysts in the conversion of *p*-coumaric acid indicates the analogy in the performances of the two systems. However, in the homogeneous system an induction time was observed. This effect was interpreted suggesting that in the homogeneous catalyst the initial Fenton mechanism involves the formation of a hydroperoxo complex, while during the course of the reaction the mechanism changes to a " $\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+}$ " cyclic route as a consequence of the change of the formation of reaction products which substitute water molecules in the coordination sphere of the copper ions. This change in the mechanism explains the presence of an induction time and the turnover frequency (TOF) increase by a factor about four after the induction time. However, when the copper ions are completely complexed by organic ligands, such as at the end of the reaction (e.g. after 4 h of reaction), the copper complex become inactive, because the hydroxyl radicals, when generated, react with the ligands itself being quenched.

The oxide ligand effect on copper ions in the solid catalyst avoids the change of the reaction mechanism which occurs in the homogeneous case. This is further supported by a different trend in the byproduct formation during the first half an hour. In particular there is a change in the first attack on the *p*-coumaric acid molecule which can be either the hydroxylation of the aromatic ring, leading to caffeic acid, or the attack on the double bond of the lateral chain leading to the formation of 4-hydroxybenzaldehyde.

A change in the TOF and efficiency in the use of  $\text{H}_2\text{O}_2$  on increasing the concentration of copper was also noted and interpreted in terms of increased probability of reaction of the short-lived hydroxyl radicals with organic species by increasing the copper concentration. In fact, the hydroxyl radical may be transferred to a second copper complex *via* two or three solvent water molecules, resulting in an effective increase of the diameter of action of the hydroxyl radicals.

Differences between the homogeneous and heterogeneous catalyst were noted regarding the effect of the presence of dissolved oxygen in solution which promotes the TOC removal in the latter case, while reduces the activity in the homogeneous case. The effect was interpreted in terms of effect of oxygen in converting  $\text{Cu}^+$  ions in solution (homogeneous case), but also of effect as mediator for the generation of  $\text{Cu}^+$  in the heterogeneous case.

Finally, the characterization of Cu(2)PILC by UV-Visible diffuse reflectance during the reaction evidences the possible formation of a surface peroxo adduct coordinated to a copper dimer, but also confirm the stability of the heterogeneous catalyst in the reaction.

In conclusion, notwithstanding the analogies in the catalytic performances, it may be concluded that effectively the homogeneous and heterogeneous copper-based catalysts are two different classes of Fenton-like catalysts.

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#### References

- [1] G. Centi and S. Perathoner, in *Catalysis* (J.J. Spivey Ed., Royal Society of Chemistry Pub.: Cambridge U.K.), 18 (2005) 46.
- [2] G. Centi and S. Perathoner, *La Chimica e L'Industria* (Milan), 83 (2001) 43.
- [3] S. Perathoner and G. Centi, *Top. Catal.* 33 (2005) 207.
- [4] R-C. Yang, M-J. Shu and S-T. Zhou, *J. Environ. Sci. (China)* 10 (1998) 176.
- [5] H. Maurer, G. Bach and J. Schneider, *Wasser, Luft und Boden* 47 (2003) 32.
- [6] J.R. Bolton, J.E. Valladares, J.P. Zanin, W.J. Cooper, M.G. Nickelsen, D.C. Kajdi, T.D. Waite and C.N. Kurucz, *J. Adv. Oxid. Techn.* 3 (1998) 174.
- [7] S. Abate, G. Centi, S. Melada, S. Perathoner, F. Pinna and G. Strukul, *Catal. Today* 104 (2005) 323.
- [8] S. Melada, F. Pinna, G. Strukul, S. Perathoner and G. Centi, *J. Catal.* 235 (2005) 241.
- [9] G. Centi, S. Perathoner, T. Torre and M.G. Verduna, *Catal. Today* 55 (2000) 61.
- [10] G. Centi, S. Perathoner and G. Romeo, *Stud. Surf. Sci. Catal.* 135 (2001) 5156.
- [11] (a) K. Fajerweg and H. Debellefontaine, *Appl. Catal. B: Env.*, 10 (1996) L229. (b) K. Fajerweg, J.N. Foussard, A. Perrard and H. Debellefontaine, *Water Sci. Technol.*, 35 (1997) 103.
- [12] F. Larachi, S. Levesque and A. Sayari, *J. Chem. Technol. Biotechnol.* 73 (1998) 127.
- [13] N. Frini, M. Crespin, M. Trabelsi, D. Messad, H. Van Damme and F. Bergaya, *Appl. Clay. Sci.* 12 (1997) 281.
- [14] J. Barrault, C. Bouchoule, K. Echachoui, N. Frini-Srasra, M. Trabelsi and F. Bergaya, *Appl. Catal. B: Env.* 15 (1998) L269.
- [15] (a) J. Barrault, M. Abdellaoui, C. Bouchoule, A. Majeste, J.M. Tatibouet, A. Louloui, N. Papayannakos and

- N.H. Gangas, *Appl. Catal. B: Env.*, 27 (2000) L225. (b) E. Guélou, J. Barrault, J. Fournier and J.-M. Tatibouët, *Appl. Catal. B: Env.*, 44 (2003) 1. (c) J.-M. Tatibouët, E. Guélou and J. Fournier, *Top. Catal.*, 33 (2005) 225.
- [16] E.V. Kuznetsova, E.N. Savinov, L.A. Vostrikova and V.N. Parnon, *Appl. Catal. B: Env.* 51 (2004) 165.
- [17] (a) C. Catrinescu, C. Teodosiu, M. Macoveanu, J. Mische-Brendlé and R. Le Dred, *Water Res.* 37 (2003) 1154. (b) M. Neamtu, C. Zaharia, C. Catrinescu, A. Yediler, M. Macoveanu and A. Kettrup, *Appl. Catal. B: Env.* 48 (2004) 287. (c) M. Neamtu, C. Catrinescu and A. Kettrup, *Appl. Catal. B: Env.* 51 (2004) 149.
- [18] J. Guo and M. Al-Dahhan, *Ind. Eng. Chem. Res.* 42 (2003) 2450.
- [19] R. Lloyd, P.M. Hanna and R.P. Mason, *Free Rad. Biol. Med.* 22 (1997) 885.
- [20] H. Gallard, J. De Laat and B. Legube, *Rev. Sc. l'Eau.* 12 (1999) 713.
- [21] N. K. Urbański and A. Berêsewicz, *Acta Biochim. Polonica* 47 (2000) 951.
- [22] (a) B. Ensing, F. Buda, P.E. Blöchl and E.J. Baerends, *Angew. Chem. Int. Ed.*, 40 (2001) 2893. (b) B. Ensing, F. Buda, P.E. Blöchl and E.J. Baerends, *J. Phys. Chem. Chem. Phys.*, 4 (2002) 3619. (c) B. Ensing, F. Buda and E.J. Baerends, *J. Phys. Chem. A*, 107 (2003) 5722.
- [23] F. Haber and J. Weiss, *J. Proc. R. Soc. London* 147 (1934) 332.
- [24] W.C. Bray and M.H. Gorin, *J. Am. Chem. Soc.* 54 (1932) 2124.
- [25] (a) G. Centi, G. Giordano, P. Fejes, A. Katovic, K. Lazar, I. Marsi, J.B. Nagy, S. Perathoner and F. Pino, *Stud. Surf. Sci. Catal.*, 154 (2004) 2566. (b) G. Centi, S. Perathoner, F. Pino, R. Arrigo, G. Giordano, A. Katovic and V. Pedulà, *Catal. Today*, 110 (2005) 211.
- [26] S. Caudo, G. Centi, C. Genovese and S. Perathoner, *Appl. Catal. B: Env.*, (2005) accepted.
- [27] J. Bandara, V. Nadtochenko, J. Kiwi and C. Pulgarin, *Water Sci. Technol.* 35 (1997) 87.
- [28] B. Ensing, PhD Thesis (Chemistry in Water. First Principles Computer Simulations), Vrije Univ. Amsterdam, The Netherlands (2003).
- [29] Y.-J. Zhagn, Y.-X. Gao, Y. Zhang, M. Yang, D.-S. Wang and C.-F. Du, *Huanjing Huaxue* 24 (2005) 361.
- [30] G.R. Rao and B.G. Mishra, *Mater. Chem. Phys.* 89 (2005) 110.
- [31] S.A. Yashnik, Z.R. Ismagilov and V.F. Anufrienko, *Catal. Today* 110 (2005) 310.
- [32] C. Lorain, G. Guyot and M. Bolte, *J. Chimie Phys. et de Physico-Chimie Biol.*, 81 (1984) (4) 243. .
- [33] A. Karaliota, O. Kretsi and C. Tzougraki, *J. Inorg. Biochem.* 84 (2001) 33.
- [34] S. Fox, A. Nanthakumar, N. Wei, N.N. Murthy and K.D. Karlin, *Pure Appl. Chem.* 65 (1993) 2235.