Review

Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity

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ABSTRACT

This review article explored the catalytic degradation of phenol and some phenols derivates by means of advanced oxidation processes (AOPs). Among them, only the heterogeneous catalyzed processes based on catalytic wet peroxide oxidation, catalytic ozonation and catalytic wet oxidation were reviewed. Also selected recent examples about heterogeneous photocatalytic AOPs will be presented.

In details, the present review contains: (i) data concerning catalytic wet peroxide oxidation of phenolic compounds over metal-exchanged zeolites, hydrotalcites, metal-exchanged clays and resins. (ii) Use of cobalt-based catalysts, hydrotalcite-like compounds, active carbons in the catalytic ozonation process. (iii) Activity of transition metal oxides, active carbons and supported noble metals catalysts in the catalytic wet oxidation of phenol and acetic acid.

The most relevant results in terms of catalytic activity for each class of catalysts were reported.

Contents

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1. Introduction

Removing pollutants from industrial process waters and wastewaters is becoming an important area of research as the amount and quality of freshwater available in the world continues to decrease due to growing water demands and/or long periods of drought. Increasingly stricter wastewater discharge standards continue to be introduced worldwide in an effort to reduce the environmental impacts of industrial processes. Chemical and petroleum industries generate a wide variety of highly toxic organic wastes. Among organic pollutants phenol and phenol derivates, used as raw materials in petrochemical, chemical and pharmaceutical industries, have received increased attention in the last years due to their toxicity. Some of the most toxic members of phenol compounds are the chlorinated and nitro-substituted phenols that are used as pesticides and anti-bacterials.

The un-substituted phenol is usually taken as a model compound for advanced wastewater treatment studies. Several technologies are available to remove industrial organic wastes, such as biological, thermal and chemical treatments. Conventional biological processes represent an environmentally friendly way of treatment with reasonable costs, however, they are not adequate to treat non-biodegradable wastewaters and, usually, require a long residence time for micro-organisms to degrade the pollutants. Among biological treatments, biodegradation of phenol in fluidized bed bioreactors has received considerable attention because of the superior performance and some inherent advantages compared to suspended biomass reactors [1]. Thermal treatments present many drawbacks, such as considerable emission of other hazardous compounds. Chemical treatments, which include flocculation, precipitation, adsorption on activated carbon, air stripping or reverse osmosis, are not resolving requiring a post-treatment [2].

Alternative pollutants destructive technologies are advanced oxidation processes (AOPs).

AOPs are characterized by a common chemical feature: the capability of exploiting the high reactivity of HO$^\bullet$ radicals in driving oxidation processes which are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants. Contaminants are oxidized through four different reagents: ozone, hydrogen peroxide, oxygen and air or their combination. These procedures may also be combined with UV radiation.

To choose the most appropriate technology some aspects, such as the concentration and nature of the pollutants and the volume of wastewater, must be considered.

Moreover, an integrated process combining AOP, as a preliminary treatment, with an inexpensive biological process, represents an interesting opportunity from an economical point of view [3].

AOPs constitute a promising technology for the treatment of wastewaters containing refractory organic compounds. Catalytic wet air oxidation (CWAO) is one of the most important advanced oxidation processes. AOPs include also many others techniques, such as methods based on ultrasound [4], plasma [5] and electro-hydraulic discharge [6] along with processes based on hydrogen peroxide (H_2O_2 + UV, Fenton, photo-Fenton and Fenton-like processes), photolysis, photocatalysis and processes based on ozone (O_3, O_3 + UV and O_3 + catalyst) [7].

Among the various AOPs processes proposed in the literature for the treatment of wastewaters containing refractory organic compounds, the present review will focus on the heterogeneous catalytic abatement of phenol and of some phenol derivates. Although several reviews on degradation of organic pollutants have been published in the last decades, the present work would summarize some AOPs technologies focusing only on heterogeneous catalytic degradation of phenol and of some phenol derivates highlighting the catalysts activity and reaction conditions.

Oxidation of phenol furnishes more hydroxylated aromatic compounds that can be oxidized to quinones while further oxidation give a complex mixture of organic compounds as reported schematically in Fig. 1.

2. Catalytic wet peroxide oxidation

Wet peroxide oxidation processes using hydrogen peroxide as the oxidant have emerged as a viable alternative for the wastewater treatments of medium-high total organic carbon concentrations. Hydrogen peroxide does not form any harmful by-products, and it is a non-toxic and ecological reactant. Moreover, although hydrogen peroxide is a relatively costly reactant, the peroxide oxidation compares very favourably to processes that use gaseous oxygen. The lack of a gas/liquid boundary removes mass-transfer limitations and the hydrogen peroxide acts as a free-radical initiator, providing
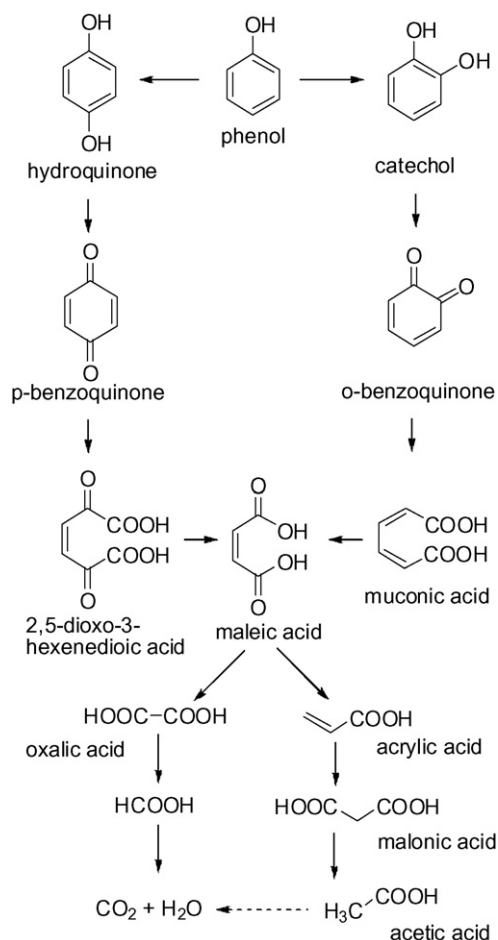

Fig. 1. Simplified scheme for phenol oxidation.

OH• radicals that promote the degradation of organics. This leads to reduce residence times and enables conversion under milder conditions. However, to enhance the decomposition of hydrogen peroxide to hydroxyl radicals the use of a catalytic system is highly desirable. Although the use of AOPs has been recently reviewed [7] with particular attention to the degradation of chlorophenols, in the present review the Fenton reaction based on the use of hydrogen peroxide combined with metal salts will be briefly introduced.

The system containing hydrogen peroxide and Fe(II) salts that in water solution form hydroxyl radicals following the reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^\bullet$$
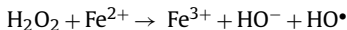
is known as the Fenton's reagent, which finds wide application for wastewater treatment [8,9]. The oxidizing efficiency of the Fenton reagent is the highest for pH ranging from 2 to 5 and for molar ratio about 1:1. The mechanism of this reagent has not been fully explained because of the variety of Fe(II) and Fe(III) complexes, numerous radical intermediate products and their consecutive reactions. A significant role is played by the formation of Fe(III) ions, which decompose H_2O_2 and produce $HO_2^\bullet$ radicals:

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2^\bullet$$

In the solution of H_2O_2 and Fe(II) salts, organics (RH) are oxidized during radical chain reactions. The main agents oxidizing and propagating the reactions are HO• radicals:

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet$$

$$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet$$
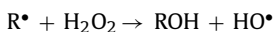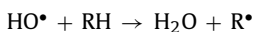
HO• radicals also decompose H_2O_2 producing $HO_2^\bullet$ radicals:

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$$
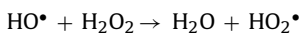
In the reaction of R• radicals with Fe(III) ions, carbocations R^+ may be formed, while in conditions involving Fe(II) ions, carbanions may occur. The kinetic chain is terminated by reactions between radicals.

The major problem of these Fenton-type homogeneous catalytic systems is the tight pH control as well as the production of additional toxic wastes, which need to be treated.

For these reasons, there has been a considerable interest in the development of heterogeneous catalysts for the oxidation of wastewater streams.

Here, we have focused the attention on different kind of supported transitions metals ions: metal-exchanged zeolites, hydrotalcite-like compounds, metal-exchanged/clays and resins.

2.1. Metal-exchanged zeolites

Zeolites are inorganic microporous and microcrystalline materials capable of complexing small and medium-sized organic molecules. Relatively few works describe the use of zeolitic materials containing metal active species tetrahedrally coordinated into the zeolitic framework for catalytic abatement of water pollutants (Table 1).

The catalyst Fe/ZSM-5 has been reported as a promising system for the treatment of phenolic aqueous wastes in presence of H_2O_2, allowing total elimination of phenol and significant total organic carbon (TOC) removal under mild working conditions [10]. Moreover, this system remains active after successive runs. The Fenton-type decomposition of hydrogen peroxide over Fe/ZSM-5 was later reported [11]. Studies about hydrogen peroxide decomposition and phenol oxidation were carried out using Cr(III), Fe(III), Bi(III), Ni(III) and Zn(III) complexes of *N,N′*-bis(salicylidene)propane-1,3-diamine (Fig. 2) encapsulated in
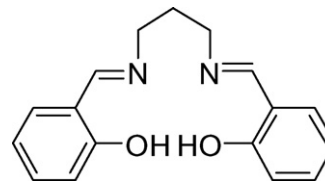

Fig. 2. Structure of *N,N′*-bis(salicylidene)propane-1,3-diamine.

Y-zeolite [12]. Cr(III), Fe(III) complexes gave the best results, however, degradation of phenol was not good. Authors concluded that the oxidation of phenol solely depended on the nature of the central metal ion present in the encapsulated complex and not on the H_2O_2 decomposition ability of the catalyst.

Degradation of phenol was also studied with immobilized Fe(III)-HY as stable and efficient photo-Fenton catalyst (Fig. 3) [13]. Different loadings of Fe(III) ions were immobilized on HY zeolite by impregnation and calcination. The effect of Fe loadings, hydrogen peroxide concentration and pH were studied. The results show that 0.25 wt.% Fe(III)-HY was efficient in the degradation of phenol at pH 6.

In a different work a series of Fe-containing zeolitic materials, prepared by different methods, have been tested as heterogeneous catalysts for the oxidation of phenolic solutions with hydrogen peroxide, under mild conditions [14]. Fe-TS-1 catalysts were synthesized through hydrothermal crystallization of wetness-impregnated Fe_2O_3-TiO_2-SiO_2 xerogels. Moreover, other Fe-modified zeolitic materials were prepared and tested. Fe-TS-1 zeolite with a moderate Fe content (76 Si/Fe molar ratio) showed the best results in terms of catalytic activity and loss of active species into the aqueous solutions. The stability of Fe species was shown to be strongly dependent on the Fe environment into the zeolitic framework, the synthetic route, and the temperature of the treatment.

Oxidation of phenol was also carried out with copper-modified zeolite (CuY-5) in wet hydrogen peroxide. The catalyst was prepared by ionic exchange from the protonic form of the commercial HY-5 zeolite. The process was performed within the temperature range from 50 to 80 °C and at atmospheric pressure. Other operating variables were: hydrogen peroxide concentration
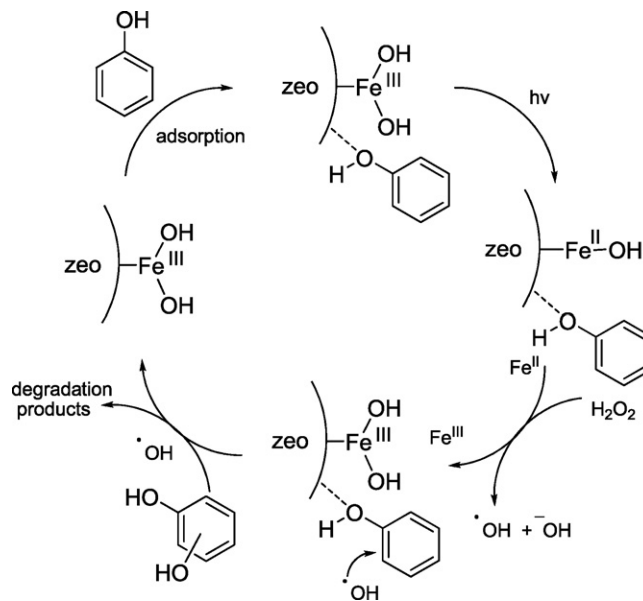

Fig. 3. A representation of photo-Fenton degradation of phenol over Fe(III)-HY [13].

Table 1
Catalytic wet peroxide oxidation of phenol substrates over metal-exchanged zeolites

Catalyst	Phenol conversion and/or TOC removal (%)	Conditions	References
Fe-aerosil 200	60 (17) TOC	Phenol 0.069 M, H_2O_2 stoichiometric ratio 1.5, catalyst 0.35 g/L, 180 min, 70 °C, pH 2.5	[10]
Fe-ZSM-5	77 (21) TOC	As above	[10]
Fe-aerosil 200	65 (19) TOC	As above, pH 3.5	[10]
Fe-ZSM-5	81 (17) TOC	As above, pH 3.5	[10]
Fe-ZSM-5	100 (46) TOC	As above, catalyst 1.5 g/L pH 3.5	[10]
[Cr(salpn)]-Y	15	Phenol 4.7 g, H_2O_2 1.2 g (30%), catalyst 0.025 g, 80 °C, 5 h	[12]
[Fe(salpn)]-Y	24	As above	[12]
[Bi(salpn)]-Y	5	As above	[12]
[Ni(salpn)]-Y	<5	As above	[12]
[Zn(salpn)]-Y	<5	As above	[12]
Fe(III)-HY	>99	Phenol 10^{-4} M, pH 6, H_2O_2 10^{-3} M, UV, 60 min	[13]
Fe-TS-1 (1) Fe 0.64 wt.%	64 TOC	Initial TOC phenol 765 ppm, H_2O_2 stoichiometric, catalyst 0.6 g/L, air pressure 1 MPa, 120 min, 100 °C	[14]
Fe-TS-1 (2) Fe 1.18 wt.%	66 TOC	As above	[14]
Fe-TS-1 (3) Fe 4.43 wt.%	70 TOC	As above	[14]
Fe-silicalite	79 TOC	As above	[14]
Fe-ZSM-5	68 TOC	As above	[14]
Fe-NaY	78 TOC	As above	[14]
Fe-USY	67 TOC	As above	[14]
Fe-ZSM-5 (by ion exchange)	54 TOC	As above	[14]
CuY-5	50	Phenol 0.01 M, H_2O_2 0.03 M, w_{cat} 0.1 g dm^{-3}, 180 min, 50 °C	[15]
CuY-5	70	As above 60 °C	[15]
CuY-5	80	As above 70 °C	[15]
CuY-5	80	As above 80 °C	[15]
Cu/ZSM-5 by hydrothermal synthesis	92	Phenol 0.01 M, H_2O_2 0.1 M, w_{cat} 0.1 g dm^{-3}, 180 min, 80 °C	[16]
Cu/ZSM-5 by hydrothermal synthesis	85	As above 70 °C	[16]
Cu/ZSM-5 by hydrothermal synthesis	75	As above 65 °C	[16]
Cu/ZSM-5 by hydrothermal synthesis	68	As above 60 °C	[16]
Cu/ZSM-5 by hydrothermal synthesis	46	As above 55 °C	[16]
Cu/ZSM-5 by hydrothermal synthesis	36	As above 50 °C	[16]
Cu/ZSM-5 by ion-exchange synthesis	96	Phenol 0.01 M, H_2O_2 0.1 M, w_{cat} 0.1 g dm^{-3}, 180 min, 80 °C	[16]
Cu/ZSM-5 by ion-exchange synthesis	81	As above 70 °C	[16]
Cu/ZSM-5 by ion-exchange synthesis	70	As above 65 °C	[16]
Cu/ZSM-5 by ion-exchange synthesis	56	As above 60 °C	[16]
Cu/ZSM-5 by ion-exchange synthesis	33	As above 55 °C	[16]
Cu/ZSM-5 by ion-exchange synthesis	20	As above 50 °C	[16]

For each catalyst or catalysts group only some experimental conditions and the corresponding phenol degradation or TOC removal are reported for a qualitative comparison.

(0.008–0.254 mol dm^{-3}) and catalyst loadings (0.05–0.4 g). The initial phenol concentration was 0.01 mol dm^{-3}. Good results were obtained at 70–80 °C, complete phenol conversion was achieved in 150 min when the oxidant supplied for the reaction was close to the stoichiometric amount for phenol oxidation. The amount of copper leached during the test (after 3 h) was 4.8%, minimal but not negligible. The results show that the used catalyst entirely eliminated phenol and could be reused in successive runs, without significant loss of activity [15]. The influence of different methods of Cu/ZSM-5 preparation on the catalytic performances, in terms of phenol conversion and metal leaching, was addressed in a recent paper [16]. The activity and stability of Cu/ZSM-5 catalyst prepared by direct hydrothermal synthesis resulted higher than the activity of the catalyst by ion exchange.

Since the degradation of phenol furnishes a mixture of carboxylic acids, the catalytic wet oxidation with hydrogen peroxide of diluted formic, acetic and propionic acid solutions were also mentioned in the present review. A study of catalytic wet peroxide oxidation of carboxylic acids was undertaken using a Fe(III)-containing zeolite, Fe/ZSM-5 and the catalytic results were compared with the behaviour of homogeneous Fe(III) catalysts in the same experimental conditions [17]. A comparison of the reactivity of heterogeneous and homogeneous Fenton-type catalysts showed that the solid catalyst has a higher rate of conversion of the propionic acid as well as a lower sensitivity with respect to pH. Indeed, a maximum activity in propionic acid conversion was observed around a pH of 4, precipitation of iron hydroxide occurring at higher pH values. However, the solid Fe(III) catalyst showed two main drawbacks: a higher rate of hydrogen peroxide decomposition to water and oxygen was observed as well as some leaching of iron, especially at high reaction temperature.

As an advantage aspect of this approach, metal-exchanged zeolites are easily prepared, although no complete phenol removal was achieved.

2.2. Hydrotalcite-like compounds

Hydrotalcite-like compounds, which are known also as layered double hydroxides or anionic clays, represent a group of important inorganic materials usable in many applications. The structure of the hydrotalcite-like compounds is very similar to that of brucite $Mg(OH)_2$, in which each magnesium cation is octahedrally surrounded by hydroxyls. Their chemical composition can
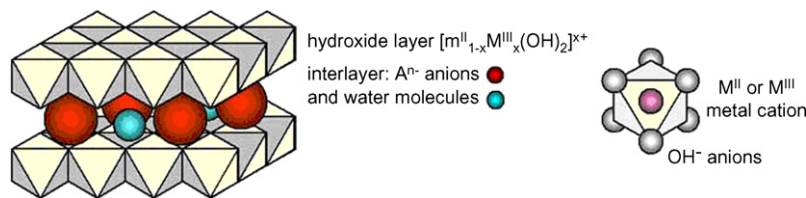
Fig. 4. Layered crystal structure of hydrotalcite-like compounds.

be expressed by the general formula $M_{1-x}^{II}M_x^{III}(OH)_2A_{x/n}^{n-}\cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent metal cations and A^{n-} is an n-valent anion, respectively. These compounds have a layered crystal structure composed of positively charged hydroxide layers $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}$ and interlayers containing anions and water molecules (Fig. 4). The value of x represents a portion of trivalent metal cations substituted in hydroxide layers and usually corresponds to $0.20 < x < 0.35$. Hydrotalcite-like compounds exhibit anion-exchange properties, i.e. anions in the interlayers may be exchanged for the other ones. At temperatures of approximately 300–500 °C, hydrotalcite-like compounds are decomposed to form mixed oxides of M^{II} and M^{III} metals. In aqueous solutions, a rehydration of these mixed oxides takes place, which is accompanied by recovering of the layered hydrotalcite structure and incorporating of the anions from solution into interlayers. This unique property of hydrotalcite-like compounds can be employed for preparation of compounds intercalated with various anions or in removal of anions from solutions. The often used group name "hydrotalcite-like compounds" is related to the mineral hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$). There are some other natural minerals and a great number of synthetic compounds with an analogous layered crystal structure combining various M^{II} and M^{III} metal cations in hydroxide layers and various anions intercalated in the interlayers.

Hydrotalcite-like compounds of general formula $CuM^{II}AlCO_3$, where $M^{II} = Co^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+} and Fe^{2+}, were synthesized by coprecipitation and characterized with XRD and IR. These materials were studied in the phenol hydroxylation by hydrogen peroxide in liquid phase [18] (Table 2). It was found that the un-calcined compounds have higher activities than those calcined. $CuAlCO_3$-

HTLcs with Cu/Al ratio of 2, 3 and 4 were prepared and used in order to study the effect of the M(II)/M(III) ratio. Results showed that phenol conversion increased with the Cu/Al ratio. However, HTLcs with higher ratio cannot be synthesized. The catalyst having Cu/Al = 3 efficiently oxidized phenol, giving high yields of the corresponding diphenols. A reaction mechanism was also proposed. Authors hypothesized that H_2O_2 might first adsorb on the surface of the layered structure of $CuM^{II}AlCO_3$ and then get one electron from Cu^{2+} ions to produce Cu^{3+}, $HO^\bullet$ and HO^-. $HO^\bullet$ can further react with phenol to produce diphenols.

Catalytic hydroxylation of phenol over ternary hydrotalcites containing Cu, Ni and Al with different $(Cu+Ni)/Al$ ratios was carried out, leading to the formation of catechol and hydroquinone [19]. The influence of various reaction parameters, such as reaction temperature, pH, solvent and hydrotalcites calcination temperatures (150, 400, 600, 800 °C, respectively) was investigated. The best results were obtained over the samples $[Ni_{0.14}Cu_{0.61}Al_{0.25}(OH)_2](CO_3)_{0.13}\cdot 0.96H_2O$ and $[Ni_{0.30}Cu_{0.38}Al_{0.32}(OH)_2](CO_3)_{0.16}\cdot 1.23H_2O$ labelled as CuNiAl3-5 and CuNiAl2-1, respectively. Authors attributed this high activity to the large concentration of copper in the former catalyst, while to a larger specific surface area in the latter catalyst. Moreover, a decrease of the copper concentration of the catalyst having a similar $(Cu+Ni)/Al$ atomic composition decreased the activity. Both catalysts showed higher activity at 65 °C. Higher temperatures decreased the conversion of phenol because of the competitive thermal decomposition of H_2O_2. The higher activity observed at pH 5 was ascribed to a better stabilization of the hydroxyl radical. Among the calcined samples, hydrotalcites treated at 800 °C exhibited the maximum activity, although their activities were lower

Table 2
Catalytic wet peroxide oxidation of phenol substrates over hydrotalcite-like compounds

Catalyst	Phenol conversion (%)	Conditions	References
CuMgAlCO$_3$	41	Cu/M^{II}/Al = 1.5/1.5/1, 60 °C, 1 h, pH 7, phenol/H$_2$O$_2$ (molar ratio) 1:60, phenol 0.5 g, catalyst 0.05 g	[18]
CuZnAlCO$_3$	38	As above	[18]
CuCoAlCO$_3$	45	As above	[18]
CuNiAlCO$_3$	47	As above	[18]
CuCuAlCO$_3$	53	As above	[18]
CuAlCO$_3$ (Cu/Al 2/1)	47	As above	[18]
CuAlCO$_3$ (Cu/Al 3/1)	53	As above	[18]
CuAlCO$_3$ (Cu/Al 4/1)	56	As above	[18]
CuAlCO$_3$ (Cu/Al 3/1)	48	50 °C	[18]
CuAlCO$_3$ (Cu/Al 3/1)	38	40 °C	[18]
CuAlCO$_3$ (Cu/Al 3/1)	28	30 °C	[18]
CuNiAl2-1	22	Phenol/H$_2$O$_2$ (mol) 2.0, catalyst 10 mg, 65 °C, 2 h pH 5	[19]
CuNiAl3-5	24	As above	[19]
CuNiAl2-1	40	As above, phenol/H$_2$O$_2$ (mol) 1.0	[19]
CuNiAl2-1	56	As above, phenol/H$_2$O$_2$ (mol) 0.5	[19]
CuNiAl3-5	41	As above, phenol/H$_2$O$_2$ (mol) 1.0	[19]
CuNiAl3-5	61	As above, phenol/H$_2$O$_2$ (mol) 0.5	[19]
Mg$_2$Al-FePcTs	88 (catechol)	Borate buffer pH 10.0, 30 °C, 0.1% catalyst/catechol ratio, H$_2$O$_2$ 3% wt., 2 h	[20]
Mg$_3$Al-FePcTs	73 (catechol)	As above	[20]
Mg$_4$Al-FePcTs	63 (catechol)	As above	[20]

For each catalyst or catalysts group only some experimental conditions and the corresponding phenol degradation or TOC removal are reported for a qualitative comparison.

than those of fresh samples, probably due to textural modifications induced by the high temperature.

An other important investigation deals with the use of Mg-Al hydrotalcite-like materials ($Mg_{(1−x)}Al_x(OH)_2(CO_3)_{x/2}·nH_2O$ with $x = 0.33$, 0.25 and 0.20) as supports for the immobilization of Fe(III) tetrasulfonated phthalocyanine (FePcTs) [20] (Fig. 5). The so obtained HT-FePcTs materials were applied in the oxidation of catechol, using hydrogen peroxide as oxidant. The catechol conversion was 63%, 73% and 88% for the materials containing HTs with $x = 0.20$, 0.25 and 0.33, respectively, indicating that the activity of HT-FePcTs materials was improved when the Al^{3+} content in the HTs increases. The influence of the Al^{3+} content in the materials reactivity was a remarkable result. Moreover, the HT-FePcTs materials showed an enhanced catalytic activity and longevity, compared to the homogeneous counterpart. These catalytic tests associated to the adsorption studies showed that the μ-oxo complex of the FePcTs, mainly adsorbed on the HTs with $x = 0.25$ and 0.33, seems to be the active species in catechol oxidation. These findings suggest that a cooperative effect take place in the HT-FePcTs materials, showing that HTs do not act as an inert support. These findings motivate the use of HT-FePcTs materials as heterogeneous catalysts in other phenol oxidation reactions, as for example, in the degradation of aromatic pollutants as chlorinated phenols. A heterogeneous catalyst with redox sites in which the host seems to play some influence, improving its catalytic activity, is particularly suitable due to the increasing interest for the use of environmentally friendly procedures in catalysis. Hydrotalcite-like compounds are also easily prepared and present the advantage of being synthesized with different M(II)/M(III) metals. However, also for these catalysts no complete phenol removal was obtained.

2.3. Metal-exchanged clays

Fe(III)-exchanged and pillared montmorillonite were used as catalysts for the degradation of 4-nitrophenol in the presence of hydrogen peroxide. The influence of different types of catalysts, their amount and the hydrogen peroxide concentration were investigated. Preliminary investigations, using different catalysts, about the effect of the dissolved Fe(III) on the reaction rate showed that only in the case of PILC-Fe and PILC-(Al-Fe) was the decomposed amount of 4-nitrophenol much lower than that observed in the heterogeneous process. This indicates that the surface contribution of the Fe clay is the controlling factor. At optimal conditions, a solution containing 10^{-3} M of 4-nitrophenol and 10^{-2} M of hydrogen peroxide was degraded in less than 6 h in the presence of 1 g/L of mixed Al-Fe pillared montmorillonite. Approximately, 3 mol of H_2O_2 per mole of 4-nitrophenol were required to remove all aromatic intermediate compounds from the solution [21] (Table 3). Al-Fe and Al-Cu modified clays were prepared from two natural montmorillonites and employed in the phenol oxidation with hydrogen peroxide in water [22]. The catalysts were efficient in phenol elimination under mild experimental conditions (atmospheric pressure, room temperature and small quantities of hydrogen peroxide) without considerable leaching of metal ions. The clays modified with Fe achieved high conversions of phenol and TOC thus showing to be very selective towards the formation of CO_2. Catalytic wet peroxide oxidation of phenol by pillared clays containing Al-Ce-Fe was also performed [23]. The catalysts were very efficient in diluted aqueous media under mild experimental conditions reaching high mineralization level. The incorporation of Ce in the solids showed a favourable effect in the pillaring of the materials and enhanced the catalytic activity of the solids. The most active catalysts (AlCeFe (10%) and AlFe (10%)) showed a tendency to reach the maximum TOC degradation (55%) after 120 min due to the accumulation of very refractory by-products such as acetic, propionic

and formic acids. The low iron leaching (<0.3 ppm) indicated that the active phase of these catalysts are strongly fixed to the support. The use of mixed Al-Cu pillared clays for catalytic wet peroxide oxidation of phenol was also reported [24]. New mixed (Al-Cu)-pillared clays were prepared from a crude bentonite sample by two discrete procedures: (a) a classical 'D' method by which Al or (Al, Cu) nitrate solutions, hydrolyzed with NaOH, are added to a 2% clay suspension and (b) a 'P' method where the clay powder is directly dispersed in the pillaring solution. Copper content resulting from the 'P' method was higher. The copper content and preparation procedure strongly influence the catalytic activity. The good interaction between copper and alumina at the surface of the catalyst seems responsible of an increased phenol oxidation activity through a heterogeneous oxidation mechanism. Copper 'solubilization' was low, showing that copper species were not simply dispersed over the clay surface. Five successive batch reactions were carried out with the same catalyst sample without any change of the reaction rate. The solution obtained after the catalyst filtration was inactive for the phenol oxidation.

Extrudates of Al-Fe pillared clay catalyst suitable for packed-bed operations were evaluated for wastewater treatment via a wet oxidation process employing hydrogen peroxide as the oxidant. The reaction was carried out in a semi-batch reactor under rather mild conditions. Operational parameters were studied such as rotation speed, temperature (25–90 °C), catalyst loading (0–10 g/L), phenol concentration (100–2000 ppm), input hydrogen peroxide concentration (0.15–0.6 mol/L). Under these conditions, the Al-Fe pillared clay catalysts achieved a total elimination of phenol and significant TOC removal. In addition, a quantitative intermediate products identification (catechol, benzoquinone, hydroquinone, oxalic acid, acetic acid) was performed. To neglect the external mass-transfer resistance the rotation speed was kept at 800 rpm. The phenol oxidation rate increased with temperature, but destruction rate of H_2O_2 also increased at high temperature. A good compromise was found at 70 °C. Studies on catalyst loading showed that the reaction took place to a significant extent both in the liquid phase and on the catalyst surface. Reactions were faster when the initial phenol concentration was lower. This catalyst can be used several times without any change in its catalytic properties. Hence, it would be a promising catalyst for industrial wastewaters treatments. Kinetic models were developed by formulating the reaction rate in two kinetic expressions that separately consider the homogeneous and heterogeneous contributions [25]. Excellent results were also obtained using mixed Al-Fe pillared clays as catalysts for oxidation of organic compounds in water by hydrogen peroxide. Using rather mild conditions (atmospheric pressure, $T \leq 70$ °C) and with a low excess (20%) of hydrogen peroxide, phenol was rapidly converted, mainly to CO_2, without significant catalyst leaching. The Al-Fe pillared clay catalyst (called FAZA) can be used several times without any change of its catalytic properties. Low amount of Fe leached from the catalyst [26].

The properties of copper-based pillared clays (Cu-PILC) were studied and compared with those of the analogous iron-based clays (Fe-PILC) in the wet hydrogen peroxide catalytic oxidation of model phenolic compounds (*p*-coumaric and *p*-hydroxybenzoic acids, Fig. 6). These two catalysts show comparable performances in all these reactions, although they showed some differences in the rates of the various steps of reaction. In particular, Cu-PILC showed a lower formation of oxalic acid (main reaction intermediate) with respect to Fe-PILC. Both catalysts showed no leaching of the transition metal differently from other copper-based catalysts prepared by wetness impregnation on oxides (alumina, zirconia) or ion-exchange of clays (bentonite) or zeolite ZSM-5 [27].

Recently, a photocatalytic oxidation of organic pollutants on titania-clay composites has been reported. TiO_2/Ca-

Table 3
Catalytic wet peroxide oxidation of phenol substrates over metal-exchanged clays

Catalyst	Phenol conversion and/or TOC removal (%)	Conditions	References
(Al-Fe)-PILC	90 (4-nitrophenol)	Catalyst 1 g/L, 4-nitrophenol 10^{-3} M, 5 h, H_2O_2 10^{-2} M	[21]
(Al-Fe)-PILC	80 (4-nitrophenol)	As above, H_2O_2 10^{-3} M	[21]
(Al-Fe)-PILC	20 (4-nitrophenol)	As above, H_2O_2 5×10^{-4} M	[21]
(Al-Fe)-PILC	10 (4-nitrophenol)	As above, H_2O_2 10^{-4} M	[21]
B-Cu[0]	15	Phenol 100 mL, 5×10^{-4} M H_2O_2 stoichiometric (14 equiv), catalyst 0.5 g, 20 °C, 3 h	[22]
B-Cu[10]	37 (0) TOC	As above	[22]
B-Fe[50]	100 (50) TOC	As above	[22]
B-Fe[100]	96 (45) TOC	As above	[22]
R-Cu[0]	15	As above	[22]
R-Cu[10]	70 (5) TOC	As above	[22]
R-Fe[50]	100 (66) TOC	As above	[22]
R-Fe[100]	100 (70) TOC	As above	[22]
Al-Fe(10%)-PILC	100 (50) TOC	Phenol 47 ppm, 25 °C, pH 3.7, 4 h, H_2O_2 0.1 M	[23]
Al-Ce-Fe(10%)-PILC	100 (54) TOC	As above, 2 h	[23]
Al-Ce-Fe(5%)-PILC	100 (52) TOC	As above, 2 h	[23]
Al-Ce-Fe(1%)-PILC	100 (55) TOC	As above, 4 h	[23]
Al-Ce-PILC	100 (51) TOC	As above, 4 h	[23]
Al-PILC	100 (39) TOC	As above, 4 h	[23]
Natural clay (calcined)	48 (5) TOC	As above, 4 h	[23]
(Al-Cu)-PILC, method P Cu 0.39%	60	Phenol 100 mL, 5×10^{-4} M, H_2O_2 excess, catalyst 0.5 g, 18 h	[24]
(Al-Cu)-PILC, method D Cu 0.16%	20	As above	[24]
(Al-Fe)-PILC	70	Phenol 500 ppm, catalyst 6.6 g/L, H_2O_2 0.3 M, 150 min, 25 °C	[25]
(Al-Fe)-PILC	87	As above, 50 °C	[25]
(Al-Fe)-PILC	96	As above, 70 °C	[25]
(Al-Fe)-PILC	99	As above, 90 °C	[25]
(Al-Fe)-PILC	100	Phenol 100 ppm, catalyst 6.6 g/L, H_2O_2 0.3 M, 60 min, 70 °C	[25]
(Al-Fe)-PILC	40	As above, phenol 1000 ppm	[25]
(Al-Fe)-PILC	10	As above, phenol 2000 ppm	[25]
(Al-Fe)-PILC	61	Phenol 500 ppm, catalyst 0 g/L, H_2O_2 0.3 M, 150 min, 70 °C	[25]
(Al-Fe)-PILC	85	As above, catalyst 3.3 g/L	[25]
(Al-Fe)-PILC	100	As above, catalyst 10 g/L	[25]
(Al-Fe)-PILC	50	Phenol 500 ppm, catalyst 6.6 g/L, H_2O_2 0.15 M, 60 min, 70 °C	[25]
(Al-Fe)-PILC	95	As above, H_2O_2 0.6 M	[25]
(Al-Fe)-PILC	99	As above, H_2O_2 3.75 M	[25]
(Al-Fe)-PILC	100 (78) TOC	Phenol 100 mL, 5×10^{-4} M H_2O_2 stoichiometric (14 equiv), catalyst 1.0 g, 70 °C, 2 h	[26]
(Al-Fe)-PILC	100 (72) TOC	As above, catalyst 0.5 g, 40 °C, 4 h	[26]
(Al-Fe)-PILC	100 (67) TOC	As above, catalyst 1.0 g, 25 °C, 4 h	[26]
(Al-Fe) -PILC	100 (63) TOC	As above, catalyst 0.5 g, 25 °C, 4 h	[26]
Cu-PILC	100 p-coumaric acid	Catalyst 0.5 g, 30 min, 70 °C, H_2O_2 (35%) 0.3 mL	[27]
Fe-PILC	100 p-coumaric acid	As above	[27]
Cu-PILC	83 (TOC) p-coumaric acid	As above, 240 min, H_2O_2 2 mL	[27]
Fe-PILC	77 (TOC) p-coumaric acid	As above, 240 min, H_2O_2 2 mL	[27]
Cu-PILC	100 p-hydroxybenzoic acid	Catalyst 0.5 g, 30 min, 70 °C, H_2O_2 (35%) 0.3 mL	[27]
Fe-PILC	100 p-hydroxybenzoic acid	As above	[27]
Cu-PILC	81 (TOC) p-hydroxybenzoic acid	As above, 240 min, H_2O_2 2 mL	[27]
Fe-PILC	73 (TOC) p-hydroxybenzoic acid	As above, 240 min, H_2O_2 2 mL	[27]
(Al-Fe)-PILC	70 (TOC) hydroxytyrosol	Total phenol concentration 0.5 g/L, catalyst 0.5 g/L, 25 °C, pH 5 H_2O_2 0.02 M, 254 nm, 24 h	[29]
(Al-Fe)-PILC	31 (TOC) tyrosol	As above	[29]
(Al-Fe)-PILC	32 (TOC) p-hydroxyphenylacetic acid	As above	[29]
(Al-Fe)-PILC	52 (TOC) p-hydroxybenzoic acid	As above	[29]
(Al-Fe) -PILC	50 (TOC) vanillic acid	As above	[29]
(Al-Fe)-PILC	86 (TOC) caffeic acid	As above	[29]
(Al-Fe)-PILC	28 (TOC) p-coumaric acid	As above	[29]
(Al-Fe)-PILC	58 (TOC) ferulic acid	As above	[29]

For each catalyst or catalysts group only some experimental conditions and the corresponding phenol degradation or TOC removal are reported for a qualitative comparison.
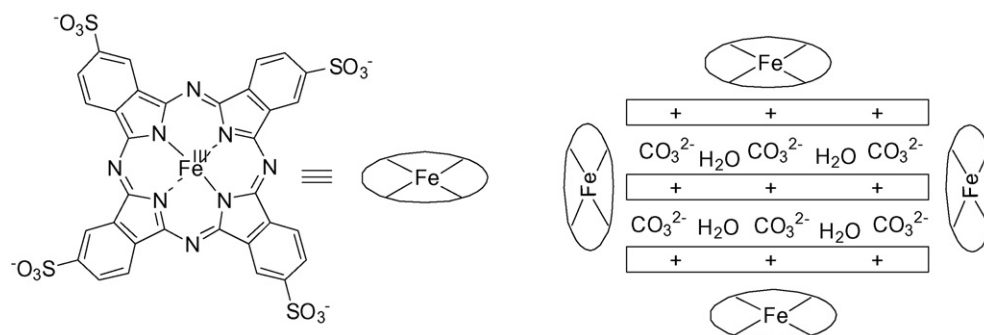
Fig. 5. Representation of the idealized adsorption of FePcTs on the surface of HTs [20].

montmorillonite composites were prepared by wet grinding in an agate mill. Positively charged TiO_2 nanoparticles are bound to the surface of the negatively charged montmorillonite layers via heterocoagulation. The clay mineral was used as adsorbent and support for the photooxidation process. Aqueous solution of 0.5 mM phenol was degraded by irradiation with UV–vis light ($\lambda = 250$–440 and 540–590 nm) in suspensions of TiO_2-clay composites having 0%, 25%, 50%, 65%, 80% and 100% TiO_2/Ca-montmorillonite composition. It was established that aqueous phenol solution was degradated at significantly higher efficiency on TiO_2/Ca-montmorillonite composite than on pure TiO_2 (ΔTOC normalized to unit weight of TiO_2 was 392 ppm for 25%TiO_2/Ca-mont. and 143 ppm for pure TiO_2) [28].

Fig. 6. Phenolic compounds used in refs. [27,29].

Aluminium-iron pillared montmorillonite (Al-Fe)PILC was used as catalyst for the wet hydrogen peroxide photodegradation of a mixture of eight phenolic compounds as model of olive mill wastewater. Important percentages of phenol abatement (86% and 70%) were achieved after 24 h of the o-diphenolic compounds caffeic acid and hydroxytyrosol, respectively. Monophenolic compounds tyrosol, p-hydroxyphenylacetic acid and p-coumaric acid were the most resistant [29]. Clays show the advantage of being naturally available and metal-exchanged clays are easily prepared to give catalyst that showed very good performances in terms of phenol conversion and TOC removal.

2.4. Metal-exchanged resins

The use of inorganic metal salts supported over resins recently has been applied for oxidation of phenolic substrates in aqueous solution (Table 4). A Fe(III)-resin supported catalysts has been reported as an effective catalysts for phenol oxidation giving almost 100% phenol conversion [30]. Resin used was a macro-porous weak acidic cation-exchange resin (Purolite C-160). The reaction temperature affected the activity, being excellent at 80 °C while low conversion was observed at 40 °C. Also initial pH values significantly affect the activity, which decreased at high pH (9) similarly to the Fenton-like mechanism. The oxidation rate of Fe(III)-resin catalyst system was dominated by the formation of OH$^\bullet$ radical and showed a significant influence on phenol decomposition. The activity of catalyst did not change with increasing the pollutant concentration in the range of 500–2000 mg/L.

The catalytic properties of Fe(III)-resin for oxidation of pentachlorophenol (PCP) with hydrogen peroxide in aqueous solution and soil suspension were also investigated [31]. The resin used was an acrylic-based macroporous weak-acid cation exchanger containing carboxylic groups (Purolite C-106). The results showed that the oxidation of PCP in aqueous medium depends on the amount of hydrogen peroxide and on the temperature, the best performance being obtained with 0.5% Fe (III)-resin catalyst at 80 °C in presence of 0.1 M H_2O_2. Moreover, it was demonstrated that the Fe(III) catalyst could be reused for at least six cycles in PCP oxidation in soil solutions at pH $\geq$5 without any loss in efficiency, leaching of Fe occurring at lower pH.

The oxidation of hydroquinone [H_2Q] to p-benzoquinone was investigated over Cu(II) ions immobilized on resins in presence of H_2O_2 [32,33]. The resin used was a terpolymer of acrylonitrile, vinyl acetate and divinylbenzene obtained by suspension polymerization. The ion exchangers with aminoguanidyl ligands were prepared by aminolysis using aminoguanidine carbonate or hydrazine followed by thioureaethyl iodide (Figs. 7 and 8). Cu(II) loading was in the range 0.11–0.32 mmol/g.
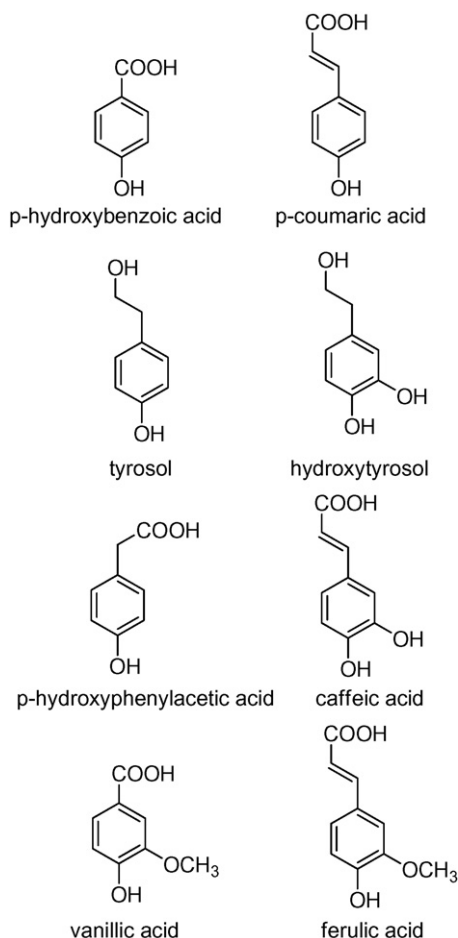
Table 4
Catalytic wet peroxide oxidation of phenol substrates over metal-exchanged resins

Catalyst	Phenol conversion (%)	Conditions	References
Fe^{3+}-resin (Fe^{3+} 275 mg/g)	100	Phenol 1000 mg/L, H_2O_2 0.1 M, catalyst 3 g, pH 3 or 5 or 7, 80 °C, 30 min	[30]
Fe^{3+}-resin	10	As above, pH 9	[30]
Fe^{3+}-resin	100	As above, phenol 500 mg/L	[30]
Fe^{3+}-resin	<10	As above, phenol 2000 mg/L	[30]
Fe^{3+}-resin	<10	As above, 60 °C	[30]
Fe^{3+}-resin (Fe^{3+} 10 mmol/g)	95 pentachlorophenol (PCP)	PCP 100 mg/L, catalyst 0.5% (w/v), H_2O_2 1 M, 80 °C, 60 min	[31]
Fe^{3+}-resin	100 (PCP)	As above, catalyst 1% (w/v)	[31]
Fe^{3+}-resin	60 (PCP)	PCP 100 mg/L, catalyst 0.5% (w/v), H_2O_2 0.05 M, 80 °C, 60 min	[31]
Fe^{3+}-resin	100 (PCP)	As above, H_2O_2 0.1 M	[31]
Fe^{3+}-resin	100 (PCP)	As above, H_2O_2 0.2 M	[31]
Fe^{3+}-resin	35 (PCP)	PCP 100 mg/L, catalyst 0.5% (w/v), H_2O_2 0.1 M, 50 °C, 120 min	[31]
Fe^{3+}-resin	70 (PCP)	As above, 60 °C	[31]
Fe^{3+}-resin	80 (PCP)	As above, 70 °C	[31]
Fe^{3+}-resin	95 (PCP)	As above, 80 °C	[31]
KA-62a (Cu^{2+} 0.90 mmol/g)	55 hydroquinone (H_2Q)	H_2O_2:hydroquinone ratio 1.4:1, hydroquinone:Cu(II) ratio 10:1, H_2O_2 0.00556 M, hydroquinone 0.004 M, 80 min, 35 °C	[32]
KA-B1 (Cu^{2+} 0.31 mmol/g)	44 (H_2Q)	Hydroquinone:H_2O_2 ratio 1:1, hydroquinone:Cu(II) ratio 10:1, H_2O_2 0.046 M, hydroquinone 0.004 M, pH 5, 80 min, 35 °C	[33]
KA-A2 (Cu^{2+} 0.32 mmol/g)	65 (H_2Q)	As above	[33]
KA-A3 (Cu^{2+} 0.22 mmol/g)	90 (H_2Q)	As above	[33]
KA-A4 (Cu^{2+} 0.19 mmol/g)	80 (H_2Q)	As above	[33]
KA-C1 (Cu^{2+} 0.11 mmol/g)	55 (H_2Q)	As above	[33]

For each catalyst or catalysts group only some experimental conditions and the corresponding phenol degradation or TOC removal are reported for a qualitative comparison.
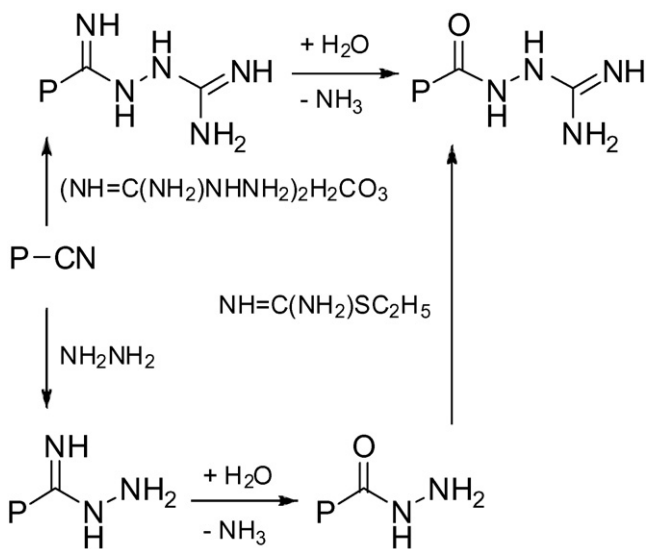

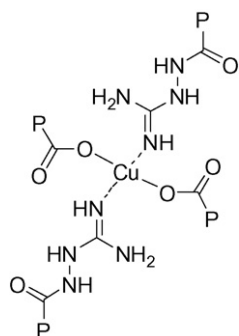**Fig. 7.** Synthesis of resin reported in ref. [33].

Fig. 8. Structure of Cu(II) complexes with aminoguanidyl ligands on resin reported in refs. [32,33].

It was found that the activity of Cu(II) ions immobilized was influenced by many parameters, such as hydroquinone/Cu(II) ratio, hydrogen peroxide concentration, pH. The optimal [H_2Q]:[Cu(II)] ratio was 10:1. Using the H_2Q excess in relation to Cu(II) results in higher loss of H_2Q (yield = 53.45%). Similar reaction yield was also achieved using the following [H_2Q]:[Cu(II)] ratios: 5:1, 7.5:1 and 20:1. It seems that the reoxidation of active centres proceeds with low rate in comparison with reduction rate. On the other hand, H_2Q molecules could not reach active centres because of their too large accumulation at the surface of catalyst. In case of low [H_2Q]:[Cu(II)] ratio, authors supposed that the majority of active centres were not used in reaction. Cu(II) loading influenced the H_2Q oxidation degree. The H_2Q loss is higher for smaller Cu(II) loading. It was shown that reaction degree of H_2Q (loss of H_2Q) increases with increase of pH. For pH 4.3, the highest loss of H_2Q was observed after 10 min of reaction. After 60 and 80 min, the loss of H_2Q was lower. This could be the effect of formation of by-product—Q(OH)$_2$ [32].

The catalysts were also tested in the presence of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate. Application of ionic liquid was pointless due to its insignificant effect on yield of reaction, environmental pollution and high price [33].

Resins can be synthesized in many different ways, giving different kind of support, however, depending on the type of support or ligand such resins may be expensive. Moreover, being the support constituted by an organic backbone, it could be also degradated under strongly oxidizing condition.
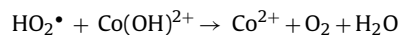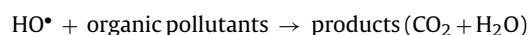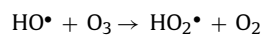
3. Catalytic ozonation

Ozone, a powerful oxidizing agent (under acidic conditions $E(O_3/O_2) = 2.07$ V), is effective for the mineralization of refractory organic compounds. However, it reacts slowly with aromatic organic compounds and, in many cases, it does not cause the complete oxidation. In presence of a catalyst and or in combination with UV or H_2O_2, the ozonation process is more efficient in the degradation of organic compounds and many studies concern-

ing purification treatment and recovery of polluted water have been reported [7,34–40]. Ozonated water is not harmful for most of the organism, therefore, ozonation finds application for drinking water disinfection, bacterial sterilization and, generally, for organic compounds degradation [41,42], however, its application to wastewater treatment is limited due to the high energy demand [7]. On the other hand, the ozonation as a pre-treatment process to transform refractory compounds into substances to be removed by conventional methods appears more economically attractive [43].

The ozonation process constitutes an AOP and is generally characterized by the production of HO• radicals. A typical homogeneous catalytic ozonation involves the use of O_3 and iron salts [9] or coupled with UV radiation, or H_2O_2 [7,40,44]. The ozonation process may proceed in two different ways depending on the pH conditions: direct reaction of molecular ozone with pollutants or indirect reaction through HO• radicals formation [45]. At low pH, the direct and selective reaction of molecular ozone with specific functional groups occurs (namely, electrophilic, nucleophilic or dipolar addition reactions), while at basic conditions ozone decomposes yielding HO• radicals [7].

Heterogeneous catalytic ozonation dating back from the 1970s [46] is now, again, attracting interest. The major advantage of a heterogeneous over a homogeneous catalytic system is the ease of catalytic retrieval from the reaction media. However, the stability and durability of the catalyst under operating condition is important. Leaching of the catalytic active species or poisoning of the active sites or fouling of the catalyst surface by intermediate reaction products are important factors, which determine the stability and durability of the catalyst.

During the last decade, many studies have been focused on the removal of refractory organic compounds from water such as phenol, hydrocarbons, carboxylic acids, etc. [35,44,47–50]. Co-based catalysts, such as Co/SiO$_2$ [51] or CoO$_x$/Al$_2$O$_3$ [52] have been used in ozone decomposition studies. The samples containing highly dispersed Co^{2+} species over the silica surface [51] have been recognized as the most efficient systems for the degradation of organic pollutants by ozone through a redox process:

$$Co^{2+} + O_3 + H_2O \rightarrow Co(OH)^{2+} + HO^\bullet + O_2$$

$$HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2$$

$$HO^\bullet + organic\ pollutants \rightarrow products\,(CO_2 + H_2O)$$

$$HO_2^\bullet + Co(OH)^{2+} \rightarrow Co^{2+} + O_2 + H_2O$$
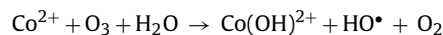
In the case of CoO$_x$/Al$_2$O$_3$ catalyst [52], the high oxidation activity in presence of ozone has been ascribed to the high content of active and mobile oxygen which strongly depends on the preparation method.

Even if cobalt oxides have shown high catalytic activities, to our knowledge, very few works deal with aqueous heterogeneous catalytic ozonation with cobalt oxide catalysts. One of these studies dealt with the removal of carboxylic acids, such as formic acid with different catalysts supported on activated carbon or SiO$_2$ [53].

In a more recent work, ozone and a cobalt catalyst supported over alumina have been used to oxidize oxalic acid from water at acidic pH [54]. Despite the high catalytic efficiency, the catalyst leached some cobalt into the water. As a result, the removal of oxalic acid was due to both heterogeneous and homogeneous catalytic ozonation.

Therefore, the attainment of active and stable catalysts for catalytic ozonation of organic pollutants in water is still a challenge.

3.1. Some recent investigations on catalytic ozonation

Among recent researches on phenol catalytic ozonation, the results obtained by our group [55] are presented (Table 5). Four series of cobalt-based catalysts, bare oxides Co$_3$O$_4$ and CoO, CoO$_x$-CeO$_2$ mixed oxides, CoO$_x$ supported over alumina and alumina-baria and CoMgAl and CoNiAl hydrotalcites have been synthesized and investigated for the oxidative degradation of phenol in the presence of ozone [55,56].

The two hydrotalcite-like compounds, labelled as CoMgAl and CoNiAl, have, respectively, the following composition: Co(39.9 wt.%)/Mg(19.7 wt.%)/Al(40.4 wt.%) corresponding to atomic ratio Co/Mg = 0.8 and CoMg/Al = 1, and Co(34.4 wt.%)/Ni(34.2 wt.%)/Al(31.4 wt.%) corresponding to atomic Co/Ni and CoNi/Al = 1.

Usually, after 1 h, phenol almost disappeared, while hydroquinone, pyrocathecol and 1,4-benzoquinone were present in small amount. Oxalic acid was formed as the main product of phenol oxidation. Accordingly, during the reaction the pH value decreased from a starting value of 5.0 to ∼2.5 (depending on the catalyst). After 4 h oxalic acid was the only detectable product by HPLC.

Over bare oxides, characterized by low surface area and big crystallites, poor results of TOC removal % were obtained after 1 and 4 h, respectively. A degradation of 11% was found over CoO that remained as low as 21% after 4 h of reaction. A higher phenol mineralization was obtained employing Co$_3$O$_4$ (22% after 1 h). The mixed oxides CoO$_x$-CeO$_2$ gave also scarce results.

Then, we moved the attention on the behaviour of alumina and alumina-baria cobalt catalysts. These samples contain very low amount of cobalt active specie (1 or 3 wt.% of Co) with respect to pure oxides. The reaction with Co(3 wt.%)Al$_2$O$_3$ gave after 1 h a TOC removal of 16% that increased to 42% after 4 h. Oxidation reaction with Co(1 wt.%)Al$_2$O$_3$ and Co(1%)/Al$_2$O$_3$-BaO gave higher TOC removal (after 4 h 55% and 57%, respectively). Co(3 wt.%)/Al$_2$O$_3$BaO gave still better results. After 1 h, the degradation was as high as 39%, reaching 74% in 4 h. Finally, we tested the two hydrotal-

Table 5
Catalytic ozonation of phenol substrates

Catalyst	TOC removal (%)	Conditions	References
Co(1 wt.%)Al$_2$O$_3$	55	Phenol 100 mL, 0.0055 M, catalyst 100 mg, 25 °C, 4 h, O$_3$ production 0.6 g/h	[55]
Co(3 wt.%)Al$_2$O$_3$/BaO	74	As above	[55]
Co(1 wt.%)Al$_2$O$_3$/BaO	57	As above	[55]
COMgAl-HTLcs	58	As above, catalyst 30 mg	[55]
COMgAl-HTLcs (calcined)	57	As above, catalyst 30 mg	[55]
CONiAl-HTLcs	90	As above, catalyst 30 mg	[55]
CONiAl-HTLcs (calcined)	70	As above, catalyst 30 mg	[55]
LaTi$_{0.15}$Cu$_{0.85}$O$_3$	95	Mixture of phenols, COD 1200 ppm, pH 3, 20 °C, O$_3$ 50 mg/L	[57]

For each catalyst or catalysts group only some experimental conditions and the corresponding TOC removal is reported for a qualitative comparison.
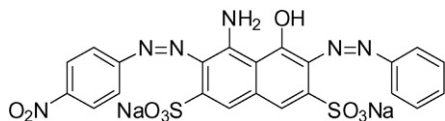
Fig. 9. Structure of naphtol blue black.

cites. According to their peculiar layered structure, which renders the active sites easily accessible, a good oxidative conversion is expected. The CoNiAl material showed the highest activity, after 4 h of reaction the TOC removal was of 90%, however, after 4 h of reaction high amount of Ni^{2+} ions were detected in solution (17 ppm). Significantly lower was the activity of the CoMgAl on which a dramatic leaching of Co was also detected (22 ppm).

Catalytic properties and stability towards leaching were investigated also on the hydrotalcites calcined at 250 °C. For both catalysts, higher cobalt leaching into the solution was observed. According to the literature [32], massive metal leaching could be due to the chelation of active metals, Co and Ni, by oxalic acid formed.

The most promising catalysts, $Co(3\,wt.\%)/Al_2O_3$-BaO, $Co(1\,wt.\%)/Al_2O_3$-BaO and $Co(1\,wt.\%)/Al_2O_3$ were also studied in three consecutive phenol oxidation reactions. The reactions were stopped after 4 h. High and stable TOC removals were obtained for $Co(3\,wt.\%)/Al_2O_3$-BaO after three cycles, quite good phenol oxidation also over $Co(1\,wt.\%)/Al_2O_3$-BaO was observed. On the contrary, less stable appears the $Co(1\,wt.\%)/Al_2O_3$ sample, showing a partial deactivation after one cycle, then the activity does not change in the successive third run. The Co-based catalysts were also tested in the oxidative degradation of aqueous solutions of naphtol blue black (Fig. 9). Results showed the superiority of $Co(3\,wt.\%)\,Al_2O_3/BaO$ (TOC removal 76% after 4 h).

Recently, ozonation of a mixture of tyrosol, syringic acid and gallic acids (Fig. 10) in the presence of a perovskite type catalyst has been also reported [57].

The perovskite $LaTi_{0.15}Cu_{0.85}O_3$ is an active and stable catalyst in ozonation processes for the treatment of refractory compounds towards the non-catalytic ozonation, while if the wastewater to be cleaned contains compounds readily attacked by ozone, there is no need of catalyst. Indeed, these phenols are quite reactive with molecular ozone so no catalyst is needed to oxidize these compounds in a few minutes. The oxidation of a mixture of these phenols was carried out in the absence and in the presence (1 g/L) of the catalyst. After 90 min no difference was observed being the TOC removal the same. This stage was followed by a second slower ad constant elimination rate. The presence of these two distinct steps was ascribed to the initial reaction of easily oxidized compounds generated from ozone attack to the parent compound molecules and first intermediates (i.e. quinones, hydroquinones, unsaturated open ring, compounds, etc.). The accumulation of ozone refractory compounds (pyruvic acid, ketomalonic acid, oxalic acid, etc.) involves a decrease on the efficacy and rate of the ozonation process. Mineralization was found favoured by temperature while pH did exert a positive effect when raising values as high as 11. The stability of the catalyst was checked by consecutive reuses of the solid
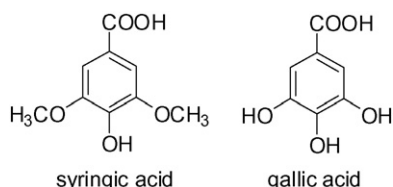
under the same operating conditions. No decrease in the activity was observed.

Among the latest investigations, catalytic ozonation of oxalic acid over activated carbon has been studied [58]. The roles of the surface chemistry of activated carbon along with the influence of the pH values (pH 3 and 7) have been investigated. Better results have been obtained at acidic pH. Although a higher pH accelerates the decomposition of ozone into more reactive species, in acidic conditions the oxalic acid has a higher affinity towards activated carbon surface and the adsorption over carbon represents an important path in the catalytic ozonation. It is worth to mention that the oxidation of oxalic acid over activated carbon leads to the complete mineralization.

As can be seen heterogeneous catalytic ozonation has allowed phenol degradation in good to high extent and also the mineralization of more recalcitrant compounds.

4. Catalytic wet oxidation (CWO)

The wet oxidation (WO), firstly patented over 50 years ago [59], uses oxygen or air to completely oxidize organic compounds to carbon dioxide and water [60]. It is a clean process not involving any harmful chemical reagent, however, being a non-catalytic process, requires high temperature and high pressure to achieve a complete oxidation in a reasonable amount of time. Therefore, the high operating costs are the limiting points of using WO.

The use of a catalyst (CWO) strongly improves the degradation of organic pollutants by using milder conditions of temperature and pressure. The recourse to a solid catalyst offers a further advantage compared with homogeneous catalysis, in principle the catalyst being easily recovered, regenerated and reused [61]. However, also, in the CWO process the stability and durability of the catalyst under operating condition must be strictly checked. Another important parameter in the oxidation processes is the mass transfer of oxygen from the gas phase to the liquid phase, which depends on the operative temperature. Studies on the effect of reactor size and reactor design have been recently reviewed, focusing on the catalytic wet oxidation both on phenol and substituted phenols [60].

In comparison with numerous studies for oxidation of pure organic liquids, relatively few investigations have been carried out for organic compounds in aqueous media. Among them, some papers deal with the oxidation of phenol solutions over transition metal oxides while some other focus on the use of noble metals supported catalysts.

4.1. Catalytic wet oxidation of phenol

4.1.1. Transition metal oxides
In Table 6, some catalytic results the on oxidation of phenol using transition metal oxides as catalytic systems are listed.

Several double layered hydroxides with hydrotalcite-like structure containing different amount of Cu(II)/Ni(II)/Al(III) cations with M(II)/M(III) ratios between 0.5 and 3.0 were prepared and used as catalysts for the wet air oxidation of aqueous solutions of phenol using air with an oxygen partial pressure of 0.9 MPa at a reaction temperature of 140 °C. Non-calcined samples were practically inactive. At calcination temperatures of 350 and 400 °C, copper catalysts showed higher initial activities than nickel ones (>90 and >70% of phenol conversion, respectively). However, the activity of them decreased continuously over time reaction, because of the elution of the active phase (CuO and/or NiO), and/or the formation of new phases due to the reaction conditions. Furthermore, nickel catalysts showed lower amounts of intermediate oxidation products such as quinones and carboxylic acids than copper ones. Experi-

Fig. 10. Phenolic compounds used in ref. [57].

Table 6
Catalytic wet oxidation of phenol substrates over transition metal oxides

Catalyst	Phenol conversion and/or TOC removal (%)	Conditions	References
Cu/Ni/Al-HTLcs	100 (99.1) TOC	$T = 140\,^{\circ}C$, $P_{O_2} = 0.9$ MPa, 2.5 h	[62]
CuO-ZnO-Al$_2$O$_3$	100	$T = 130\,^{\circ}C$, $P_{O_2} = 0.3$; 0.56 MPa, 1–2 h	[63,64]
ZnO-CuO-C-Al$_2$O$_3$	100	$T = 130\,^{\circ}C$, $P_{O_2} = 0.5$ MPa, 40 min	[65]
Bimetallic catalysts: CuO-CoO; CuO-Fe$_2$O$_3$; CuO-MnO; CuO-ZnO	>80%; 50%; 20–30%	$T = 140\,^{\circ}C$, $P_{O_2} = 900$ KPa, 0–6 h; 24 h; >96 h	[69]
CuO-CeO$_2$ prepared by sol–gel method	100	$T = 150\,^{\circ}C$, $P_{O_2} = 0.73$ MPa, 30 min	[70]
Cu/MCM-41	90 (TOC)	$T = 200\,^{\circ}C$, $P_{O_2} = 3.4$ MPa, 20 min	[71]
Mn-Ce-O composites Ce/(Ce + Mn) = 0.2–0.7	80–90 (TOC)	$T = 110\,^{\circ}C$, $P_{O_2} = 0.5$ MPa, 10 min	[72]
CeO$_2$ catalyst loading: 1 g/L, phenol conc.: 400 ppm	90% (TOC)	$T = 160\,^{\circ}C$, $P_{O_2} = 1$ MPa, 3 h	[73]
CeO$_2$/γ-Al$_2$O$_3$	~100	$T = 180\,^{\circ}C$, $P_{O_2} = 1.5$ MPa, 2 h	[74,75]
Cu promoted CeO$_2$/γ-Al$_2$O$_3$	~100	$T = 180\,^{\circ}C$, $P_{O_2} = 1.5$ MPa, 1 h	[76]
CeO$_2$-TiO$_2$	80 (TOC)	$T = 140\,^{\circ}C$, $P_{air} = 3.5$ MPa, during 100 h	[77]
Al-Fe pillared clay, catalyst loading: 6.6 g/L, phenol conc.: 500 ppm	100	$T = 130\,^{\circ}C$, $P_{air} = 1.5$ MPa, 100 min	[78]
Fe/AC	100, 80 (TOC)	$T = 127\,^{\circ}C$, $P_{O_2} = 8$ atm	[79]
Fe/AC	>80%	$T = 114\,^{\circ}C$, $P = 8$ atm	[80]
Commercial active carbons	~100	$T = 160\,^{\circ}C$, $P_{O_2} = 16$ bar	[85]
Multi-walled carbon nanotubes (MWCNTs)	100	$T = 160$, $P_{O_2} = 2$ MPa, 2 h	[86]

For each catalyst or catalysts group only some experimental conditions and the corresponding phenol degradation or TOC removal are reported for a qualitative comparison.

ments performed in an autoclave reactor showed no loss of activity for the Cu-Ni-spinel phase for three consecutive runs (sample HT[0.5/0.5/2] Cu$_{0.26}$Ni$_{0.23}$Al(OH)$_{2.98}$(CO$_3$)$_{0.45}$(NO$_3$)$_{0.10}$·2.1H$_2$O calcined at 750 °C). Some catalysts (spinel phases, obtained for the samples calcined at 1023 K) showed any loss of activity after a continuous working run of 15 days using a trickle-bed reactor [62].

Liquid-phase oxidation of phenol by oxygen was studied over a commercial catalyst containing CuO(42 wt.%)-ZnO(47 wt.%)-Al$_2$O$_3$(10%) [63,64]. The catalyst was found to be effective for the full conversion of phenol to non-toxic compounds, at the temperature of 130 °C. The rates of phenol disappearance showed that the reaction progressed auto-catalytically through a heterogeneous–homogeneous free radical mechanism. The oxidation of phenol in water in a batch autoclave was also studied over catalysts with the following composition: (35%)CuO + (65%)ZnO; (5–15%)CuO + (85–95%)Al$_2$O$_3$; (26%)CuO + (74%)Cu chromite. Moreover, in a Parr reactor the catalysts with composition: (35%)CuO + (65%)ZnO; (5–10%)Ba$_2$CO$_3$ + (<5%)C + (30–40%)CuO + (60–70%) ZnO; and (8–15%)Al$_2$O$_3$ + (1–5%)C + (35–45%)CuO + (40–50%)ZnO were tested [65]. Under certain conditions of temperature (130 °C) and oxygen pressure (300 psig) the catalyst (8–15%)Al$_2$O$_3$ + (1–5%)C + (35–45%)CuO + (40–50%)ZnO was found to be the most active. Although the present review is not devoted to the kinetic investigation of catalytic liquid-phase phenol oxidation, it is worth noting the interesting paper dealing with the oxidation of phenol to benzenedioles, benzoquinones and carbon dioxide over a proprietary catalyst containing supported copper, zinc and cobalt oxides [66]. It is believed that the liquid-phase oxidation of phenol undergoes a combined redox and heterogeneous free-radical mechanism. The apparent activation energy for catalytic phenol oxidation was found to be 139 kJ/mol. In this paper, a kinetic approach based on the Langmuir–Hinshelwood model is proposed and a bimolecular surface reaction between adsorbed reactants is considered to be the rate-controlling step. The kinetic of phenol oxidation using oxygen or air as oxidant was addressed also by using commercial supported copper oxides in a continuous trickle-bed reactor at

three temperatures (120, 140 and 160 °C) and at three partial pressures of oxygen [67]. Understanding the phenomena occurring at the catalyst surface during wet oxidation processes is complicated, requiring the characterization of intermediate products, however, it is essential to develop a resistant catalyst. Actually, the intermediates of phenol oxidation were in part identified by HPLC and so the mechanism reported in literature is often a simplified reaction scheme. A detailed investigation of the phenol degradation profile and catalyst behaviour was carried out over a Mn/Ce(7/3) composite oxide catalyst and compared with a Pt(1 wt.%) over alumina [68]. By using TPO-MS analyses a net difference was observed in the combustion behaviour of the organic deposit over the two types of catalysts. From the XPS analyses, it was found that the organic species adsorbed over Pt/alumina are mainly graphitic, while aliphatic compounds prevail over Mn/Ce.

Going on in the review, we want to mention the effectiveness of bimetallic supported catalysts, 2% of CoO, Fe$_2$O$_3$, MnO or ZnO combined with 10% CuO supported on γ-alumina, to oxidize aqueous phenol solutions using air as oxidant [69]. The oxidation was carried out in a packed-bed reactor operating in trickle flow regime at 140 °C and 900 kPa of oxygen partial pressure. Lifetime tests were conducted for 8 days. The pH of the feed solution was also varied. The results show that all the catalysts tested undergo severe deactivation during the first 2 days of operation. Later, the catalysts present steady activity until the end of the test. The highest residual phenol conversion was obtained for the ZnO-CuO/Al$_2$O$_3$, which was significantly higher than that obtained with the 10% CuO catalyst used as reference. The catalyst deactivation was found to be related to the dissolution of the metal oxides from the catalyst surface due to the acidic reaction conditions. Generally, the performance of the catalysts was better when the pH of the feed solution was increased.

The activity and selectivity of the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ catalysts prepared by co-precipitation and by sol–gel methods were studied in the catalytic wet oxidation (CWO) of phenol at 150 °C and at 7.3 bar oxygen partial pressure in a semi-batch CST reactor. It was found that activity and selectivity increase with the dispersion

of copper oxide phase on the cerium oxide. Moreover, the samples prepared by sol–gel technique were up to four times more active and about 25% more selective toward CO_2 formation than the samples prepared by co-precipitation at given reaction conditions [70]. Catalysts with different copper loading supported on mesoporous MCM-41 with surface area over $1400\,m^2/g$ were also evaluated in the catalytic wet oxidation of phenol solutions at 150 and 200 °C [71]. Mesoporous MCM-41 results a promising catalyst support for wastewater treatment: due to its characteristics, uniform pore structure and large surface area and pore volume, it can assist copper in removing phenol with high efficiency and speed. High loading of copper on MCM-41 is not necessary, as it will reduce the surface area. Cu/MCM-41 with a thin layer of copper loading should be enough to provide a high catalytic activity. The catalytic oxidation of phenol was studied also over Mn-Ce-O composite catalysts with $Ce/(Mn + Ce)$ atomic bulk ratios ranging from 0% to 100% [72]. The results showed that the catalytic activity was greatly influenced by the catalyst composition. The catalyst with Mn/Ce ratio = 6/4 was found to be the most active in reducing both phenol concentration and total organic carbon. The catalysts with $Ce/(Ce + Mn)$ ratios between 0.2 and 0.7 show high but rather constant activity, achieving ca. 80–90% removal efficiency, while pure manganese oxide was slightly active and pure cerium oxide showed virtually no catalytic activity in the chosen experimental conditions. However, in successive papers the activity of ceria was reported. The effect of catalyst loading, oxygen pressure, reaction temperature and phenol concentration on phenol conversion and TOC removal, using CeO_2 as the catalyst, was investigated. With phenol concentrations in the range of 400–2500 mg/L and oxygen pressure of 0.5 or 1.0 MPa, the optimal catalyst loading was 1.0 g/L [73]. The activity of several alumina supported ceria catalysts for the catalytic wet air oxidation of phenol was also investigated using an autoclave reactor [74]. Results indicated that the support and the Ce content are both important factors affecting phenol conversion. Using the optimal CeO_2/γ-Al_2O_3 catalyst (loading 3.0 g/L), about 100% phenol conversion was achieved after 2 h reaction at 180 °C and 1.5 MPa O_2 partial pressure. In a successive study, the oxidation of phenol over the CeO_2/γ-Al_2O_3 catalyst as a function of O_2 partial pressure, 0.5–2.0 MPa, was reported [75].

Recently, the effect of promoter addition on activity of CeO_2/γ-Al_2O_3 was assessed via the CWAO of phenol [76]. Cu promoted CeO_2/γ-Al_2O_3 catalyst was the most effective, followed by Mn, although the performance of Mn-promoted catalyst was inferior to CeO_2/γ-Al_2O_3. At 180 °C, under 1.5 MPa oxygen partial pressure the Cu-promoted catalyst ($Ce_{15}Cu_5$) produced about 100% conversion of phenol in 1 h.

The wet air oxidation of an aqueous solution of phenol was studied also over extrudates of an Al-Fe pillared clay catalyst in the temperature range of 90–150 °C and air pressure range of 0.8–2.5 MPa. The variables studied included reaction temperature, air pressure, solution pH, initial phenol concentration, and catalyst loading. The obtained findings are compared with those obtained using hydrogen peroxide oxidation [77]. It was seen that temperature strongly affects the evolution of phenol and intermediate carbon. Higher phenol removal rates were observed at higher temperatures. It was found that air could completely remove phenol within 100 min at 130 °C. A home-made Fe/activated carbon (Fe/AC) catalyst has been tested for the wet oxidation of phenol in a down-flow fixed bed reactor at relatively mild conditions (100–127 °C and P_{O_2} = 8 atm, initial pH of 3.5). Complete phenol conversion and 80% TOC removal were reached at 127 °C and $320\,g_{CAT}\,h/g_{Ph}$ [78]. The same authors in a successive article identified intermediate oxidation products of phenol oxidation over Fe/activated carbon catalyst, working at mild operating conditions (100–127 °C; 8 atm) in a trickle-bed reac-

tor [79]. Ring compounds (hydroquinone, p-benzoquinone and p-hydroxybenzoic acid) and short-chain organic acids (maleic, malonic, oxalic, acetic and formic) have been identified as intermediates.

Among the latest investigations, it is worth noting the study of phenol oxidation over CeO_2-TiO_2 mixed oxides [80]. These systems show higher activity than pure CeO_2 and TiO_2, and CeO_2-TiO_2 1/1 catalyst displays the highest activity in the CWAO of phenol. Over this catalyst, 80% TOC removal was obtained for 100 h continue reaction, at the reaction temperature of 140 °C and air total pressure of 3.5 MPa. Moreover, leaching of metal ions of CeO_2-TiO_2 1/1 particle catalyst was very low during the continuous reaction.

It is worth noting that, recently, studies concerning the catalytic wet oxidation (CWO) of a phenolic mixture in presence of hydrogen peroxide over a commercial activated carbon have been carried out [81]. This work represents an example of an integrated process which combines the Fenton reaction with a CWO with the aim to increase the efficiency of this last step. Indeed, in the case of phenolic pollutants, it has been reported that mineralization of phenols obtained by CWO [82] is higher than that obtained by using the Fenton reagents [83]. However, the abatement of the initial phenolic pollutants is quicker if Fenton reagent is used. Therefore, using a Fenton pre-treatment, with relatively low H_2O_2 dosage, the CWO can be accomplished efficiently and in milder conditions [81].

Taking advantage of both, the high phenol conversions in CWPO and the high phenol mineralization in CWAO, a CWPO-CWAO sequential treatment was successfully performed over a Fe/AC by using a fixed-bed and trickle-bed reactor in series [84]. The CWPO treatment in ambient conditions followed by a CWAO treatment in mild conditions (100 °C and 8 atm) was reported as high efficiency process for the decontamination of phenolic wastewaters.

A study dealing with the use of active carbons as catalysts for catalytic wet oxidation of phenol was reported [85]. Good results in both phenol conversion and mineralization were obtained, moreover, the main intermediate compounds were detected. Short chain acids, maleic, acetic and formic were detected, while only small amounts of oxalic acid were found. Besides the high mineralization of pollutants achieved over these active carbons, leaching of active phase is avoided, as no metal impregnation is required.

We want to highlight also the use of multi-walled carbon nanotubes (MWCNTs) as catalysts for wet air oxidation of phenol (Fig. 11) [86]. The MWCNTs modified using HCl or HNO_3-H_2SO_4 exhibit high activity and good stability. At 160 °C and oxygen pressure of 2 MPa 100% phenol conversion was achieved after 120 min of reaction.

4.1.2. Noble metal catalysts

In Table 7, some papers on oxidation of phenol using supported noble metal catalysts are listed. Among the precious metals used for phenol oxidation, ruthenium is one of the most studied since 20 years. Preliminary investigations performed 20 years ago, indicated ruthenium as the most active catalyst among the precious metals examined and ceria oxide as the most active support [87]. Ru, Pt and Rh catalysts supported on titania, ceria or active carbon were studied in the wet air oxidation of phenol and acetic acid under twenty bar of oxygen. Phenol was easily oxidized at 170 °C over Pt/CeO_2, while acetic acid was difficult to oxidize and Ru/C resulted the most efficient catalyst [88].

In a successive study, Ru/C catalysts promoted, or not, by cerium were prepared and investigated in catalytic wet air oxidation (CWAO) of phenol at 160 °C and 20 bar of O_2 and their performance (activity, selectivity to intermediate compounds) was compared with that of a reference Ru/CeO_2 catalyst [89]. Ru-CeO_2/C was the most active catalyst. However, it must be noticed that a total mineralization of phenol is never observed and significant differ-
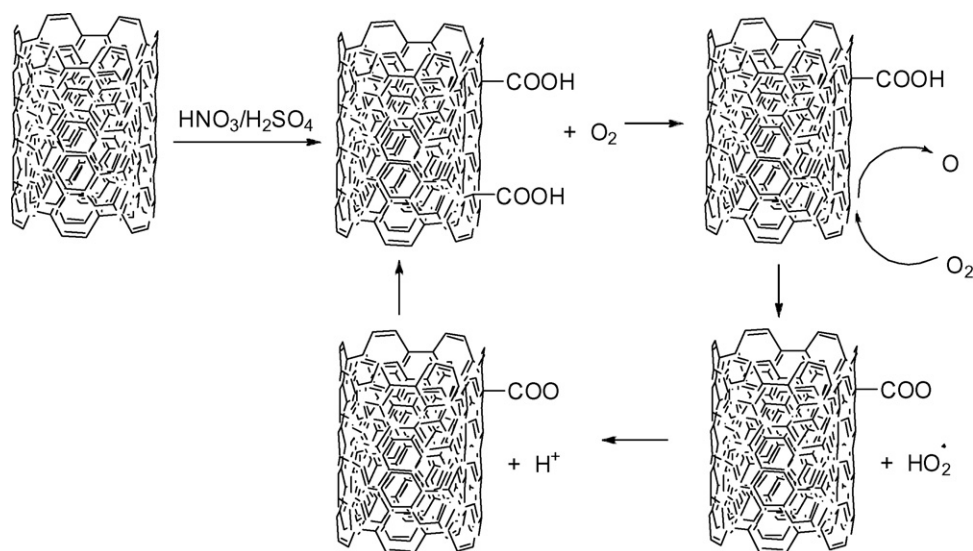
Fig. 11. Proposed mechanism producing $HO_2^\bullet$ in the CWAO of phenol over B-MWCNTs [86].

ences, in terms of C_3–C_6 organic intermediates, were observed between Ru/CeO$_2$ and the Ru carbon supported catalysts. Indeed, on carbon supported catalysts, the transformation of C_3 compounds into acetic acid was much slower than over Ru/CeO$_2$, leading to a definite accumulation in solution of C_3 compounds. Experiments of phenol oxidation were performed also over several 1%Ru/5%CeO$_2$-Al$_2$O$_3$ samples, prepared by different methods, at 140 °C and 7 atm of oxygen pressure [90]. Results indicate that performance of the catalysts is influenced by the preparation method, moreover, phenol conversions diminished with reaction time, due to the deposition of carbonaceous solids on the surface and to the transformation of the support into boehmite phase. Ruthenium catalysts were prepared by impregnation of two different pelletized supports, CeO$_2$ and ZrO$_2$-CeO$_2$ and studied for phenol oxidation in a continuous packed-bubble column reactor [91]. At 140 °C, under air pressure of 4 MPa a stable phenol conversion around 100% was obtained within 100 h of reaction.

Besides Ru, also Pt supported catalysts have received considerable attention for phenol oxidation. Wet oxidation of phenol by air or oxygen was carried out over a Pt/TiO$_2$ in a batch reactor between 150 and 200 °C, in the pressure range 34–82 atm [92]. Complete oxidation of phenol and almost complete TOC removal were achieved. Catalytic wet oxidation reactions of aqueous phenol over MnO$_2$/CeO$_2$ catalysts promoted by Pt and Ag were carried out under mild conditions (80–130 °C, 0.5 MPa O$_2$) in a batch slurry

reactor [93]. The effects of Ce addition on the wet oxidation of phenol over two Pt/Al$_2$O$_3$ catalysts, prepared by using as precursors H$_2$PtCl$_6$ and Pt(NH$_3$)$_4$Cl$_2$, respectively, were investigated [94]. The Pt catalyst prepared from the former precursor was much more active than that prepared from the latter, due to a better metal dispersion. Ceria addition lowered the activity of this sample, while improved the activity of the catalyst from Pt(NH$_3$)$_4$Cl$_2$. The catalytic wet oxidation of phenol was also studied using platinum on graphite support as a catalyst in a slurry phase continuous stirred tank reactor (CSTR) [95]. The investigation was carried out in the temperature range 120–180 °C and at total pressure of 1.8 MPa, the oxygen partial pressures varying between 0.01 and 0.8 MPa. It was found that both the oxygen load and the stoichiometric oxygen excess determine the extent of oxygen coverage on the platinum surface, which influences the reaction pathways and selectivity to CO$_2$ and H$_2$O. In a recent paper [96], the synthesis and catalytic properties of mixed platinum-containing nanoparticles stabilized in polymeric matrix of hypercrosslinked polystyrene were discussed. The catalytic system showed high activity, selectivity and stability in the phenol CWAO. The phenol oxidation was studied at various catalyst loadings, substrate concentrations and temperatures.

Several Pd, Pt, Ru-based catalysts have been used also for the oxidation of *p*-chlorophenol. Each reaction has been carried out at $T = 180$ °C and $P_{O_2} = 2.6$ MPa for 1 h (see Table 8) [97]. More-

Table 7
Catalytic wet oxidation of phenol over supported noble metal catalysts

Catalyst	Phenol conversion or TOC removal (%)	Conditions	References
Ru/CeO$_2$	94.8 (TOC)	$T = 200$ °C, $P_{O_2} = 1$ MPa, 1 h	[87]
Pt(1%)/CeO$_2$	100	$T = 170$ °C, $P_{O_2} = 20$ bar, 4 h	[88]
Ru/C	85	$T = 160$ °C, $P_{O_2} = 2$ MPa, 3 h	[89]
Ru-CeO$_2$/C	99.5	$T = 160$ °C, $P_{O_2} = 2$ MPa, 3 h	[89]
Ru-CeO$_2$	93.8	$T = 160$ °C, $P_{O_2} = 2$ MPa, 3 h	[89]
Ru/CeO$_2$-Al$_2$O$_3$, fresh catalysts	24–30, 4–5	$T = 40$ °C, $P_{O_2} = 7$ atm, 7 h, 50 h	[90]
Ru/ZrO$_2$-CeO$_2$	~100	$T = 140$ °C, $P_{air} = 4$ MPa, during 100 h	[91]
Pt/TiO$_2$	100	$T = 175$ °C, $P_{air} = 34$ atm, 30 min	[92]
Pt$_x$Ag$_{1-x}$MnO$_2$/CeO$_2$	80 (TOC)	$T = 80$ °C, $P_{O_2} = 0.5$ MPa, 1 h	[93]
Pt/Al$_2$O$_3$ prepared by using H$_2$PtCl$_6$	100	$T = 170$ °C, $P_{air} = 5.05$ MPa, 2 h; $T = 200$ °C, $P_{air} = 5.05$ MPa, 1 h	[94]
Pt-graphite	99	$T = 150$ °C, $P_{O_2} = 1.8$ MPa, 1 h	[95]
MM-HPS-Pt	100	$T = 95$ °C, O$_2$ flow rate $= 10^{-2}$ L/s, 5 h, q(substrate/catalyst concentration) $= 27.2$ mol/mol	[96]

Table 8
Catalytic wet oxidation of *p*-chlorophenol [97]

Catalyst	TOC removal (%)
Pd/activated carbon	97.5
Pd/Al$_2$O$_3$	81.8
Pd/CeO$_2$	45.4
Pt/activated carbon	97.9
Pt/Al$_2$O$_3$	91.2
Pt/CeO$_2$	50.4
Pt/Pd/Al$_2$O$_3$	84.7
Pt/Pd/Ce/Al$_2$O$_3$	68.6
Ru/activated carbon	91.8
Ru/Al$_2$O$_3$	72.4
Ru/CeO$_2$	65.7
Mn/Al$_2$O$_3$	82.5

over, recently, the catalytic wet air oxidation of 2-chlorophenol was studied over Ru/zirconia and Ru/Ce$_x$Zr$_{1-x}$O$_2$ catalysts [94,95]. Ru loaded zirconia catalysts were found to be active in the catalytic wet air oxidation (CWAO) of 2-chlorophenol (2-CP) at relatively mild temperature [98]. To optimize the reaction conditions, the effects of different operating parameters, such as the rotation speed, the reaction temperature, the total pressure, the initial concentration and the pH of the initial 2-CP solution on the catalytic activity of 3 wt.% Ru/ZrO$_2$ were evaluated. The conversion of 2-CP increases with the pH of the initial 2-CP solution. The effect of ruthenium precursor, Ru(NO)(NO$_3$)$_3$ and RuCl$_3$ was also investigated. The same authors also evaluated the activity of 2-CP wet oxidation over Ru/Ce$_x$Zr$_{1-x}$O$_2$ catalysts [99]. This study represents a new application of such ruthenium supported catalysts for the catalytic wet air oxidation of 2-CP. The results are promising, exhibiting Ru/Ce$_x$Zr$_{1-x}$O$_2$ much better performances compared to Ru/ZrO$_2$ and Ru/CeO$_2$.

4.2. Catalytic wet oxidation of acetic acid

Oxidation of phenol furnishes catechol and hydroquinone, which could be oxidized to *o*-benzoquinone and *p*-benzoquinone, according to Devlin and Harris (Fig. 2) [88,100]. Further oxidation of both products gives a complex mixture of carboxylic acids or salts (depending on pH) which are converted to carbon dioxide and water. However, these acids/salts are highly refractory to oxidation. For this reason, several studies were carried out on several carboxylic acids/salts in aqueous solution. Some results about the catalytic wet oxidation of acetic acid are here briefly reviewed. Among the first investigations performed over 20 years ago, the study concerning the complete oxidation of acetic acid over Co-Bi composite oxides catalysts is worth to be mentioned [101]. Co-Bi composite oxides with Bi contents of 10–20 mol% exhibited high activity for the oxidation of acetic acid. Temperature-programmed desorption experiments showed that the high activity of Co/Bi oxides for the oxidation of acetic acid was due partly to the strong affinity of Bi for this molecule. Ceria-containing mixed oxides, namely CeO$_2$-ZrO$_2$-CuO and CeO$_2$-ZrO$_2$-MnO$_x$, were utilized as catalysts in the oxidation of acetic acid. The incorporation of zirconia, MnO$_x$ or CuO into the fluorite structure of ceria strongly enhances the redox properties and promotes the oxidation activity [102]. The use of ruthenium supported over cerium oxide for wet oxidation of organic compounds, such as acetic acid, was reported by several authors [87,88,103–106]. Carbon supported ruthenium catalysts gave a total conversion of acetic acid into carbon dioxide between 175 and 200 °C using air as oxidizing agent [103]. The total oxidation of aqueous solutions of succinic acid (via acetic acid formation as intermediate) by air was studied in the range of temperature 180–200 °C and oxygen partial pressure of 0.3–1.8 MPa over a ruthenium/titania catalyst [104]. The beneficial effect of ceria

over ruthenium supported catalysts was investigated in the wet oxidation of acetic acid over Ru/CeO$_2$ prepared by different methods [105]. The activity was ascribed to the high mobile oxygen of the bond Ru–O–Ce. Ru and Pt catalysts prepared by using sono-chemical irradiation over mesoporous titania and zirconia oxides found application for the removal of organic pollutants from model wastewaters using the wet air oxidation process [106]. Acetic acid along with succinic and *p*-coumaric acids was used as target compounds. Ru and Pt catalysts supported over Ce, Zr, Pr-O mixed oxides have been, recently, investigated for acetic acid wet air oxidation [107,108]. It has been demonstrated that the catalytic activity depends on the ability of the support to resist to the formation of carbonates. Ce(CO$_3$)OH species were formed during the CWAO process, especially on the catalysts with high oxygen storage capacity (OSC). It was found that a moderate OSC is required to maintain a good activity. The effects of metal and oxide crystallite size were also studied by the same authors over Pt catalysts supported over cerium-based materials [109]. In particular, the sintering effect of hydrogen treatment on the catalytic performances was evaluated. It emerged that the highest conversion of acetic acid in terms of turnover frequency (TOF) values was achieved over an optimal platinum crystallite size, while there is no correlation between OSC and catalytic activity of ceria-based catalysts.

Study of CWAO of acetic acid were carried out also utilizing a monolith froth reactor, working with a two-phase bubble-train flow within the channels of the monolith and developed at the University of Tulsa, in USA [110]. The active species was platinum deposited over the alumina-washcoated channels of the monolith. The catalyzed monolith froth reactor compares well with other catalytic systems for the acetic acid oxidation, with the advantages of a monolithic catalyst (lower pressure drop, excellent mechanical stability, high surface area to volume ratio).

When no noble metal is present, such as for CeO$_2$-TiO$_2$ catalysts prepared by sol-gel method, good activity and stability in the WAO of acetic acid was observed [111]. The interaction of Ce and Ti affects the surface structural properties of the mixed oxides, increasing the activity with respect to pure ceria and titania. The optimal atom ratio Ce/Ti was found equal to 1.

5. Recent reports on real effluent treatments

Release of natural phenolic compounds from agro-industrial manufacturing processes may cause environmental pollution. Wine-distillery, olive oil extraction, table olive debittering, cork preparation, tomato processing, etc. generate liquid effluents with a high content of phenolic structures like gallic, protocatechuic, vanillic, syringic, caffeic, and ferulic acids, tyrosol, catechin, etc. In this section, will be reported several recent examples of real wastewater treatment using the reported procedure.

Ozonation in the presence and in the absence of perovskite LaTi$_{0.15}$Cu$_{0.85}$O$_3$ of three different wastewaters was reported. Wastewaters were collected from a wine distillery, from the debittering stage of olives and from an olive mill meant to olive oil production. Only in the latter case, use of the catalyst gave higher COD conversion [57].

The wet air oxidation of wastewater from olive oil mills has been demonstrated to be a feasible process to effectively reduce the levels of contamination of these effluents. Removal of toxic phenolic-type compounds is accomplished under relatively mild conditions of temperature and pressure (180 °C and 7.0 MPa total pressure). As a consequence, the oxidized wastewater shows a higher degree of biodegradability if compared to the non-treated wastewater. Experiments completed in the presence of two commercially available catalysts (platinum supported on alumina and

copper oxide supported on active carbon) showed not only an improvement in the chemical oxygen demand removal rate but also a high degree of the mineralization of the wastewater contaminant load [112].

Catalytic wet air oxidation of olive mill wastewater was also carried out using carbon supported platinum (Pt 1 wt.%) and iridium (Ir 5 wt.%) catalysts prepared by incipient wetness impregnation. Experiments were performed in a high pressure reactor at 100 and 200 °C under an oxygen partial pressure of 6.9 bar. At 100 °C, refractory organic compounds persisted even after prolonged reaction time (8 h). At 200 °C, complete total organic carbon and colour removal was obtained with the Pt/C catalyst after 8 h of reaction [113].

Copper and iron-based pillared clays (Cu-PILC, Fe-PILC) were studied in the wet hydrogen peroxide catalytic oxidation (WHPCO) of real olive oil milling wastewater. These two catalysts showed comparable performances, although the activity of the Fe-PILC was slightly better. After 4 h of reaction, the TOC abatement was about 20%, but it should be taken into account that the initial value was quite high (28,000 ppm). The poly-phenolic compounds conversion was about 45% and similar for the two catalysts [27].

Two Cu-silicalite-1 zeolite catalysts were prepared by direct hydrothermal synthesis (Na)S1 (Cu 2.25 wt.%, Si/Cu 47.1 mol/mol) and (Na)S2 (Cu 2.34 wt.%, Si/Cu 45.3 mol/mol). A Cu-pillared clay (Cu-AZA) was prepared by pillaring procedure of a clay. These catalysts were used for wet hydrogen peroxide catalytic oxidation of three samples of olive oil mill wastewaters (OOMW1, 2, 3). The Cu-silicalite-1 catalysts showed a high catalytic activity respect to the non-biodegradable compounds (poly-phenol) and also to the organic substrate. An elevated COD_{TOT} abatement was, in fact, observed for both OOMW-1 and OOMW-2. After a re-calcination treatment, the zeolites were re-used for a second reaction cycle, and they show good results. A partial copper leaching was observed, but the value of metal concentration in the treated wastewater can be settled at the accepted limit (0.4 mgCu/L). The Cu-AZA catalyst showed minor performances in TOC abatement and in the poly-phenol degradation compared to zeolitic samples, but it can be re-used for several reaction cycles, because it showed no copper leaching during the oxidation reactions [114].

(Al-Fe)PILC was used as catalyst for the wet hydrogen peroxide photodegradation of real OMW obtained by ultrafiltration of crude OMW. Almost similar results were obtained compared with the model OMW. Using 0.5 g/L of catalyst and 0.02 M H_2O_2 under UV light irradiation for 24 h, TOC removal was 40% and total phenol removal was 60% [29].

Very recently, an industrial stream-containing phenol, collected in a naphtha cracking unit of a petrochemical plant, was used to test the performance of a heterogeneous catalyst obtained from copper adsorption by an ionic-exchange resin (sulfonated styrene-divinylbenzene), followed by carbonization [115]. The catalyst was characterized before and after the catalytic tests by SEM-EDS. The industrial wastewater, with 60 mg/L phenol, was compared with a model stream (1000 mg/L phenol). Successive reactions were also carried out in order to study the catalyst deactivation. The reaction was performed at 38 °C, 1 atm, pH 6.5, using a phenol to hydrogen peroxide molar ratio of 14. The catalyst was able to remove all phenol compounds present in both streams. The catalyst did not show any deactivation in the industrial stream, but deactivated in the model stream, a fact that can be assigned to the copper leaching, as inferred by SEM-EDS. In the model stream, the high phenol concentration caused a high production of organic acids, generated by parallel reactions, which led to copper leaching. The industrial stream did not show deactivation since the amount of these acids was too low to leach copper.

6. Summary and conclusions

From the present review the following main results can be summarized:

H_2O_2 is a non-toxic and ecological reactant and in combination with an opportune catalyst easily decomposes, in a short period of time, to hydroxyl radicals producing degradation of pollutants. Although H_2O_2 is a relatively costly reactant, catalytic peroxide oxidation compares very favourably to other catalyzed processes, which use gaseous oxygen or ozonation. Taking into account data concerning wet peroxide oxidation of phenol here reviewed, it can be concluded that the extent of phenol conversion and mineralization achieved are satisfactory. Moreover, very often the used catalyst could be reused in successive runs, without significant loss of activity, although, depending on the reaction conditions, pH and temperature, some leaching of metal ions can occur. Among the numerous researches, some of the most effective data include the use of a copper-modified zeolite (CuY-5) prepared by ion-exchange: the results show that the used catalyst entirely eliminated phenol in the range of temperature within 50–80 °C and could be reused in successive runs, without significant loss of activity [15]. Moreover, the influence of the preparation methods and the use of Cu/ZSM-5 catalysts were addressed in a recent paper [16]. It is worth to be mentioned the important investigation deals with the use of Mg-Al hydrotalcite-like materials ($Mg_{(1-x)}Al_x(OH)_2(CO_3)_{x/2} \cdot nH_2O$ with x = 0.33, 0.25 and 0.20) as supports for the immobilization of Fe(III) tetrasulfonated phthalocyanine (FePcTs) [20]. Among metal-exchanged clays for catalytic peroxide oxidation the results obtained over extrudates of a Al-Fe pillared clay catalyst are promising for industrial wastewaters treatments [25–27]. Interesting results have been also obtained using Fe^{3+}-resins [30,31].

Ozone, a powerful oxidizing agent (under acidic conditions $E(O_3/O_2) = 2.07$ V), is effective for the mineralization of refractory organic compounds. However, it reacts slowly with aromatic organic compounds and, in many cases, it does not cause the complete oxidation. In presence of a catalyst and or in combination with UV or H_2O_2, the ozonation process is more efficient in the degradation of organic compounds and many studies concerning purification treatment and recovery of polluted water have been reported. The pH strongly influences ozone decomposition in aqueous solutions: the higher the pH, the higher the decomposition of ozone into more reactive species that participate in the ozonation process. Among some recent investigations on catalytic ozonation, the following should be mentioned: (i) the use of Co(3 wt.%)/Al_2O_3-BaO, Co(1 wt.%)/Al_2O_3-BaO and Co(1 wt.%)/Al_2O_3 catalysts for consecutive phenol oxidation reactions [55]. (ii) The ozonation of phenolic (a mixture of syringic, pyruvic and gallic acids) wastewaters in the presence of a perovskite type catalyst $LaTi_{0.15}Cu_{0.85}O_3$ [57]. (iii) The catalytic ozonation of oxalic acid over activated carbon [58].

The wet oxidation (WO), using oxygen or air to completely oxidize organic compounds to carbon dioxide and water, is a clean process not involving any harmful chemical reagent, however, being a non-catalytic process, requires high temperature and high pressure to achieve a complete oxidation in a reasonable amount of time. The use of a catalyst (CWO) strongly improves the degradation of organic pollutants by using a lesser amount of oxidizing agent and milder conditions of temperature and pressure. Moreover, the CWO allows the selective removal of a single pollutants or a group of similar pollutants among a complex mixture. Many efficient transition metal oxides and noble metals catalysts have been prepared in the last years and several excellent studies on the identification of the reaction mechanism during CWO of phenol have been carried out.

Some of the catalysts recently reported include: (i) multi-walled carbon nanotubes (MWCNTs) as catalysts for wet air oxidation of phenol [86]. At 160 °C and oxygen pressure of 2 MPa 100% phenol conversion was achieved after 120 min of reaction. Moreover, it is worth to note that over such systems leaching of active phase is avoided, as no metal impregnation is required. (ii) Mixed platinum-containing nanoparticles stabilized in polymeric matrix of hypercrosslinked polystyrene [96]. The catalytic system showed high activity, selectivity and stability in the phenol CWAO. (iii) Ruthenium catalysts prepared by impregnation of two different pelletized supports, CeO_2 and ZrO_2-CeO_2, and studied for phenol oxidation in a continuous packed-bubble column reactor [91]. At 140 °C, under air pressure of 4 MPa a stable phenol conversion around 100% was obtained within 100 h of reaction. Moreover, it was remarked that the Ru/ZrO_2-CeO_2 catalyst possesses the possibility of practical use. (iv) Ru/zirconia and $Ru/Ce_xZr_{1-x}O_2$ catalysts studied in the catalytic wet air oxidation of 2-chlorophenol [98,99]. Ru loaded zirconia catalysts were found to be active in the catalytic wet air oxidation (CWAO) of 2-chlorophenol (2-CP) at relatively mild temperature [98]. $Ru/Ce_xZr_{1-x}O_2$ catalysts were also evaluated in the activity of 2-CP wet oxidation by the same authors [99]. This study represents a new application of such ruthenium supported catalysts for the catalytic wet air oxidation of 2-CP. The results are promising, exhibiting $Ru/Ce_xZr_{1-x}O_2$ much better performances compared to Ru/ZrO_2 and Ru/CeO_2. (v) Ru and Pt catalysts prepared by using sonochemical irradiation, over mesoporous titania and zirconia oxides, for the removal of organic pollutants from model wastewaters using the wet air oxidation process [106]. Acetic acid, succinic and *p*-coumaric acids were used as target compounds. (vi) Ru and Pt catalysts supported over Ce, Zr, Pr-O mixed oxides, recently, investigated for acetic acid wet air oxidation [107,108]. Several of the catalysts reported have been successfully used for the treatment of real effluents.

The major advantage of the use of heterogeneous catalytic materials is their easy recovery. Unlike the homogeneous systems, these solid catalysts can be recuperated by means of a simple separation operation and reused in the next runs. In this sense, one of the principal goals of these types of processes is the development of stable heterogeneous catalysts with minimal leaching of active species under the reaction conditions. In many cases, catalysts have been reused giving reproducible results. Moreover, leaching was low in the reported catalysts being high only in selected cases [55].

In conclusion, it must be noticed also that integrated processes which combine catalytic peroxide oxidation with a CWO are suitable techniques for the degradation of phenolic pollutants in a short time and they are economically convenient. Indeed, it was reported that, using a Fenton pre-treatment with relatively low H_2O_2 dosage, the CWO can be accomplished efficiently and in mild conditions [81]. Moreover, taking advantage of both, the high phenol conversions in CWPO and the high phenol mineralization in CWAO, a CWPO-CWAO sequential treatment was successfully performed over a Fe/AC by using a fixed-bed and trickle-bed reactor in series [84]. Finally, the use of integrated processes which combine AOPs, as preliminary treatments, with biological treatments of wastewaters containing refractory compounds are effective to achieve complete degradation of pollutants and attractive from an economical point of view. As further development in this field, more active and robust catalysts, in which metal leaching is absent, will be highly desirable.

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