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Oxidation of hazardous compounds by heterogeneous catalysis based on Cu/Al₂O₃ system in Fenton-type reactions

Laura G. Covinich^a, Paola Massa^b, Rosa J. Fenoglio^b, and María C. Area^a

^aPrograma de Celulosa y Papel, Instituto de Materiales de Misiones, IMAM (UNaM-CONICET), Posadas, Argentina; ^bDepartamento de Ingeniería Química/Div. Catalizadores y Superficies, INTEMA (CONICET' UNMdP), Mar del Plata, Argentina

ABSTRACT

This review examines in detail all components involved in heterogeneous Fenton-type reactions, with special focus on copper species supported on alumina for H₂O₂ decomposition, their redox chemistry, and their practical advantages over traditional Fenton for the degradation of recalcitrant organic compounds. Several aspects for a deeper comprehension of the properties of γ -Al₂O₃ as support for catalytic applications are discussed. Iron-free systems stability after calcination and catalyst performance during the oxidation reaction are evaluated to solve the disadvantages of iron-based system. Copper species supported on alumina for H₂O₂ decomposition in Fenton-like reactions are examined, with special focus on their redox chemistry and practical advantages over traditional Fenton system for recalcitrant compounds degradation. Characterization techniques for the elucidation of the structures, compositions, and chemical properties of both the solids used in heterogeneous catalysis, and the adsorbates and intermediates present on the surfaces of the catalysts during reaction are explained. Global indicators for chemical characterization of wastewaters and measurement of catalytic efficiency are described.

KEYWORDS

Adsorbates; copper based catalyst; intermediates characterization; recalcitrant organic compounds; solid catalyst

1. Introduction

The increasing world population with growing industrial activities and consumption habits has positioned the environmental protection as a priority issue and a crucial factor for several industrial processes, which will have to meet the requirements of the sustainable development for modern societies. In order to balance the industrial activities with the environment preservation there is a global tendency to adopt rigid environmental legislation, where the well-known Green Technologies play a key role. Some chemical processes are valid options of best available technologies because they do not entail excessive cost and aspire to minimize

CONTACT Laura G. Covinich  covinich_laura@yahoo.com.ar  Programa de Celulosa y Papel, Instituto de Materiales de Misiones, IMAM (UNaM-CONICET), Félix de Azara 1552, Posadas, Argentina.

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impact. These environmentally friendly strategies minimize, or even eliminate, the use or generation of hazardous substances in the design, manufacture, and application of chemical products.^[1] An overview of these treatments is shown in Table 1.

Many wastewaters from industrial processes contain organic pollutants that are toxic and poorly biodegradable when concentration is too high for direct biological treatments. On the other hand, the concentrations of these agents are often so small that the classical recovery (such as centrifugation, flocculation, and filtration) is not economically feasible. Chemical oxidation tries to accomplish complete mineralization of the contaminants to carbon dioxide, water, and inorganics or their transformation into harmless products. These pollutants are not amenable to biological treatments and may also be characterized by high chemical stability and/or by great difficulty to be completely mineralized. In these cases, it is necessary to adopt more effective reactive systems than those used in conventional purification processes.^[20] Direct oxidation of organic contaminants in aqueous solutions can be performed under a variety of conditions, ranging from ambient conditions to supercritical water oxidation at very high temperatures and pressures.^[21] High-yield pulping wastewaters are characterized by a high organic load, low biodegradability, and the presence of iron and other metals, so that these effluents are usually managed as hazardous wastes and commonly treated by incineration (or noncatalytic chemical processes) at a high cost. However, these features also make these effluents good candidates to be treated by chemical oxidation.^[22] Energy consumption of various well-known oxidation procedures e.g. supercritical water oxidation, wet peroxide oxidation, wet oxidation, and wet air oxidation may be reduced with adaptable catalyst.^[23]

Technologies like Fenton, photo-Fenton, wet oxidation, ozonation, photocatalysis, etc., known as Advanced Oxidation Processes (AOPs) differ in the source of free radicals. AOPs with the capability of exploiting the high reactivity of hydroxyl radicals have emerged as a promising technology for the treatment of wastewaters containing refractory organic compounds.^[24] The hydroxyl HO• radical is an oxidizing species even more reactive than fluorine. Although fluorine displays the strongest oxidation potential, its application is undesired due to formation of halogenated compounds in the course of oxidation. Compared with chlorine or ozone, HO• radicals exhibit much higher oxidation potential. Moreover, HO• radicals react nonselectively with organic or inorganic species with higher rate constants (10^8 – $0^9 \text{ M}^{-1} \text{ s}^{-1}$) than molecular O₃ (1 – $10^3 \text{ M}^{-1} \text{ s}^{-1}$). The rate of HO• radical generation is of great interest when it is used to decompose toxic organic compounds in wastewater.^[25] AOP processes are widely used to treat wastewaters from several industries such as chemical, petrochemical, paint, textile, and pesticide plants, containing different organic compounds such as aromatic rings, polyphenols, halogenated compounds, resin acids, unsaturated fatty acids, compounds resulting from the decomposition process of organic nitrogen, mutagenic compounds, hydrocarbons, volatile organic compounds, pentachlorophenol (PCP), nitrophenols,

Table 1. Options of chemical treatment most used in wastewater treatment.

Treatment process	Main features	Refs.
<i>Chemical oxidation</i> Incineration	Involves complete thermal oxidation at elevated temperature. It is a useful method when treating small amounts of liquid with a high concentration of oxidizable contaminants. Otherwise, the operating costs associated with the need for an auxiliary fuel become excessive.	[2]
Wet air oxidation (WAO)	Removes organic compounds in the liquid phase by oxidizing them completely to carbon dioxide and water using an oxidant such as oxygen or air. However, one of its significant drawbacks is that high temperatures and pressures are required (more than 120°C and 10 bar) to achieve a high degree of oxidation within a reasonable time.	[3, 4]
Catalytic wet air oxidation (CWAO)	This technique is proposed to relax the WAO oxidation conditions. The addition of catalysts allows the process to be carried out at much milder conditions, improves conversion of organic pollutants that are refractory to non-catalytic oxidation, and accelerates the oxidation reaction.	[5, 6]
Supercritical water oxidation (SCWO)	Shows high efficiency for decontamination of many aqueous organic wastes in an aqueous medium, above the critical temperature and pressure of pure water (374°C and 221 bar, respectively). This technique can efficiently destroy organic substances into H ₂ O and CO ₂ (99–99.99% of conversion) at 500–650°C in 1–100 s, which are significantly short residence times.	[7]
<i>Advanced oxidation (AOP)</i> O ₃ /OH ⁻	This technique performs best at alkaline pH, due to the reaction of almost all organic and inorganic compounds with molecular ozone and oxygen radicals, including the hydroxyl radical. These phenomena are attributed to the ability of O ₃ to initiate hydroxyl radical formation at high pH. These hydroxyl radicals have an oxidation potential (2.80 V) higher than O ₃ (2.07 V) in direct reaction under acidic conditions	[8]
O ₃ /H ₂ O ₂ and O ₃ /H ₂ O ₂ /OH ⁻	Ozone treatment greatly enhances the production of hydroxyl radicals by adding H ₂ O ₂ during the reaction. This can reduce the reaction time required for organic matter transformation.	[9, 10]
O ₃ /UV and O ₃ /H ₂ O ₂ /UV	Combining ultraviolet radiation (UV) with H ₂ O ₂ results in the generation of •OH. It can lead to organic matter transformation by direct photolysis and by reaction with •OH. Therefore, these combinations have higher yields of hydroxyl, peroxy, and superoxide radicals, which synergistically accelerate the removal of organic matter from complex wastewater matrices.	[10, 11]
O ₃ /Catalyst	Ozonation is influenced by pH of the solution (high pH), composition of the solution, and temperature, but it is limited to a certain extent of mineralization. In this context, some studies have focused on heterogeneous catalytic ozonation in aqueous media, due to the enhancement of the production of hydroxyl radicals with materials such as activated carbons, zeolites, oxides, and the subsequent O ₃ economy. Efficient catalysts have been reported via different approaches, such as accelerating •OH radical production from ozone or enhancing the chemical adsorption of target pollutants on the surface of the catalyst.	[12, 13]
H ₂ O ₂ /Me ⁿ⁺ and H ₂ O ₂ /Me ⁿ⁺ /UV	These catalytic methods are based on the generation of hydroxyl radicals from hydrogen peroxide with metal ions acting as catalyst at certain pH and temperature. The generally accepted mechanism of the process proposes that hydroxyl radicals are produced while the catalyst is regenerated. It does not require highly complicated devices or pressurized systems for the oxidation process, making it technologically viable for direct application on any scale. The most studied process is	[14–17]

(Continued on next page)

Table 1. (Continued)

Treatment process	Main features	Refs.
Electro-H ₂ O ₂ /Me ⁿ⁺	Fenton, which implies the oxidation of ferrous to ferric ions to decompose H ₂ O ₂ into hydroxyl radicals. The combination of UV/Vis radiation with Fenton's reagent (photo-Fenton process) promotes the oxidation reaction yielding additional radicals by photolysis. This method is divided into four categories. In type 1, hydrogen peroxide and ferrous ions are electrogenerated using a sacrificial anode and a bubbling oxygen cathode. In type 2, a sacrificial anode is used as a source of ferrous ions and hydrogen peroxide is externally added. In type 3, ferrous ions are externally added and hydrogen peroxide is generated using a bubbling oxygen cathode. In the type 4 (the most used one), Fenton's reagent is used to produce hydroxyl radicals in an electrolytic cell, and ferrous ions are regenerated by the reduction of ferric ions at the cathode.	[18]
Sono-H ₂ O ₂ /Me ⁿ⁺	This method is a combination of ultrasound and H ₂ O ₂ with transition metals. In sonolysis, the radicals are produced through cavitation. This phenomenon includes three phases: nucleation, growth, and an adiabatic implosive collapse of a gas or vapor bubble. These phases are driven by pressure variations induced in the liquid medium due to propagation of the ultrasound wave. The •OH radicals are formed at the location of the bubble collapse. With Me ⁿ⁺ present in the medium, •OH radicals can also be generated through Fenton reactions. The micromixing by ultrasound can also increase the probabilities of interaction of radicals and organic molecules.	[19]

detergents, and pesticides, as well as inorganic contaminants such as cyanides, sulfides, and nitrites.^[26–30]

There is a need to improve current wastewater technologies for several reasons: (1) the increasing cost of wastewater treatment, (2) the severe environmental regulations, and (3) an increasing attention to Emerging Pollutant Categories of Concern (EPOC; e.g. endocrine disrupting chemicals, hormonally active agents, xenobiotics, pharmaceutically active compounds, persistent organic pollutants, etc.) and in general to effluent-derived microcontaminants and organic wastewater contaminants.^[31] Among AOPs, the use of catalysts to improve the performance of water treatment technologies is known for many years, but only in the last decade more scientific attention was given to this. Catalysts are distinguished into homogeneous (catalyst operates in the same phase where the reaction occurs) and heterogeneous (it operates in a different phase). In the case of homogeneous catalysts, every single catalytic entity can act as a single active site, which makes them intrinsically more active and selective compared to traditional heterogeneous catalysts. The heterogeneity of the surface sites is, in fact, a common feature of the solid catalysts.^[32]

Homogeneous catalysts offer some advantages over their heterogeneous counterparts. As said, all catalytic sites are accessible because the catalyst is usually a dissolved metal complex. Furthermore, it is often possible to tune the chemoselectivity, regioselectivity, and/or enantioselectivity of the catalyst. The main

disadvantage compared with heterogeneous catalysts is the difficulty to separate the reaction products from the catalyst and from any reaction solvent. This problem arises because most homogeneous catalysts are thermally sensitive and the most commonly used separation method, distillation, requires high temperatures. Other conventional processes such as chromatography or extraction also lead to catalyst loss.^[33] Organic solvent nanofiltration^[34,35] and membranes nanofiltration^[36, 37] are other widely known separation techniques. Precipitation by the formation of hydroxides is the most common method for homogeneous metal recovery. The precipitate obtained after the alkalization of the reaction media is often called the Fenton sludge. This alkaline precipitation and recycling of the metal could be a viable alternative for catalyst recovery and reuse in oxidative reactions.^[38] Unfortunately most of these catalyst recovery methods are not economically feasible for industrial application. So, the use of solid catalyst is generally preferred, which can be recovered by a simple operation and reused in the treatment process.

This review examines in detail all components involved in heterogeneous Fenton-type reactions, with special focus on copper species supported on alumina for H₂O₂ decomposition, their redox chemistry, and their practical advantages over traditional Fenton for the degradation of recalcitrant compounds.

2. Heterogeneous catalysis

2.1. Main characteristics of heterogeneous catalyst

Heterogeneous catalysts are frequently defined as solids, or mixtures of solids, which accelerate chemical reaction without undergoing changes. This definition however is too limited in scope, considering that the properties of catalysts can change significantly with use, with service lives that vary from minutes to years.^[39]

Metal oxides are the key components for a variety of catalytic reactions, functioning directly as reactive components or as supports to disperse active metal species, or as additives or promoters to enhance the rate of catalytic reactions.^[40] A heterogeneous catalyst is considered as a composite material, and is characterized by: (1) the relative amounts of components (such as active species, physical and/or chemical promoters, and supports); (2) shape; (3) size; (4) pore volume and distribution; (5) surface area. The optimum catalyst provides a certain combination of desired properties at an acceptable cost. Solid catalysts must fulfill a number of requirements, such as high activity in terms of pollutant removal, minimum leaching of active phase, stability over a wide range of pH and temperature, and a high hydrogen peroxide conversion with minimum decomposition, selectivity, lifetime, ease of regeneration, and toxicity.^[41] Therefore, catalyst design mainly consists of a suitable compromise between the desired morphological characteristics and the specifications required for a long catalyst life.^[39, 42]

The ideal surface of the particles of a solid oxide can be constituted by: (1) exposed coordinatively unsaturated cationic centers (acting as Lewis acid sites), (2)

exposed oxide species (acting as basic sites), and (3) exposed hydroxy groups arising from water dissociative adsorption (acting as Brønsted acid sites, or, alternatively, as basic sites).^[43] Surface stabilization reactions with several compounds from the environment (e.g., water and CO₂) might occur. This would limit the number of coordinatively unsaturated centers, causing the formation of new surface species such as hydroxy groups and surface carbonates. However, unsaturated centers at the surface can be regenerated by desorption of adsorbed water (and CO₂) under heating.^[44] In a typical catalyst, the role of active sites is the direct activation of the adsorbed intermediate, as well as catalytic activity and selectivity.^[40] Activity is one of the most important characteristics and is defined as the ability to accelerate a certain reaction to a greater or lesser extent. The activity is expressed in transformed moles per second per gram of catalyst. Selectivity is another important feature that defines the direction in which the reaction will take place due to the intervention of the catalyst. This intervention will result in the increase of some products, the decrease of others, the appearance of unexpected species, etc., while minimizing the activation energy. The selectivity is expressed as the amount of reactant converted to a particular product divided by the total transformed reactant.

The loss of the catalyst activity (or selectivity) is a problem of great concern in the practice of industrial catalytic processes. A solid catalyst may be negatively affected by any of a dozen compounds present in the reaction medium, and its surface and pores may be affected by reactants, intermediates, and/or products.^[45] Deactivation is the overall result of the removal of active sites from the catalytic surface.^[46] The most common causes of deactivation are (1) poisoning, (2) fouling, (3) thermal degradation, (4) mechanical damage, and (5) corrosion/leaching by the reaction mixture.^[47]

- 1) Catalyst poisoning involves a strong chemisorption of certain species on the catalyst (interaction between a component of the reactant or products and the active sites of the catalyst). It may be reversible or irreversible; however, most poisons are irreversibly chemisorbed.^[45] Examples of poisoning can be found in reference.^[48]
- 2) Fouling is the physical deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores.^[45] Examples of fouling can be found in references.^[1,3,49]
- 3) Thermal degradation of catalysts produces the loss of catalytic surface area and can occur in all stages of the life cycle of the catalyst.^[47] It can occur as result of: a) particle growth and/or filling up of the pores (due to the phenomenon known as sintering),^[50] and b) chemical transformations of catalytic phases to noncatalytic phases.^[45] Examples of thermal degradation can be found in references.^[51,52]
- 4) Mechanical damage represents the loss of catalytic material and the loss of its internal surface area due to mechanical processes such as abrasion, mechanical-induced crushing, and erosion of catalyst particles.^[45]

- 5) Corrosion and leaching behavior of the support can affect the performance during reaction and its stability. Even if supports show good resistance to corrosion and leaching, the reaction medium can be quite corrosive.^[53] Examples of corrosion/leaching can be found in references.^[47,54,55]

The performance of metal oxides as catalysts or catalyst supports depends on their crystalline structure and textural properties. Besides the role of the surface area, the pore structure plays an important role in the catalytic activity. Mesoporous materials are preferred because they offer the advantage of avoiding the pore plugging (that often occurs in materials with micropores).^[56] The different pore sizes of specific catalysts have implications on properties concerning diffusion of reactant, site accessibility, and catalyst deactivation. In heterogeneous catalysis, conversions proceed on active sites on the surface of solid catalysts. The conversion is thus closely related to the accessible surface area of a given catalyst.^[40] The pores, which are the paths for reactants and products, influence the incorporation of active metals during preparation of the catalyst. It is proved that supports with higher pore volume render high dispersion of active phase,^[57] and that the presence of these mesopores increases the amount of accessible active sites, which improves the catalytic reactions.^[58] With features such as highly uniform channels, large surface area, and narrow pore-size distribution, the mesostructured alumina is envisaged to minimize the mass transfer resistance of reactants and products in and out of the catalyst particles.^[59] It is therefore of great importance in the preparation of porous alumina with defined structure and controllable pore size.^[60]

2.2. Influence of support's preparation method

It has long been recognized that the properties of catalysts and catalyst supports often depend on their preparation method. Several strategies were developed to obtain mesoporous alumina with high surface area, but the usual method is sol-gel synthesis, which is characterized by a high reproducibility on the results.^[61–64] The surface area of the final solids depends on the original micelle size and on the ripening (coarsening of the gel framework by dissolution and reprecipitation) and drying conditions. Due to the possibility of obtaining high-surface-area solids with homogeneous compositions and controlled porosity, sol-gel methods have been widely employed for the synthesis of mesoporous materials. The process of removing the solvent from the gel is critical and determines the textural properties of the final product. Many materials prepared by the sol-gel method, especially the aerogels, are mesoporous with large surface area and large pore volume.^[62,65] The sol-gel techniques have been widely applied for the synthesis of highly porous alumina, according to procedures directly related to that originally developed by Yoldas.^[66] For many years, the sol-gel method itself or combined with other methods has been used for catalyst supports preparation^[67,68] in order to optimize the desired properties. Since Yoldas developed the sol-gel technique, the preparation conditions of sol and gel have been extensively studied. Reaction temperature,

concentration of reactants, pH of sol (because of its great influence on the surface area of the final product), and many factors in the process from hydrolysis of aluminum alkoxide (e.g. the nature of complexation of the alkoxide determined the gel structure) to final pore structure were evaluated.^[69,70] The sol-gel process provides a new approach for preparation of these materials and offers many advantages for manufacture of catalysts, and a homogeneous mixture can be achieved even at molecular scale. Compared to other methods, throughout sol-gel technique, the chemical reactivity of the surface oxide produced can be higher. Sol-gel working temperatures are lower than others methods, and it is a very versatile technique to obtain powders of various surface area, optimal distribution of pore size, and high purity supports.^[71]

Moreover, the design of solid catalysts requires the selection of the supported metal oxide, in addition to the development of an adequate support. The classification of several metal supports according to their catalytic activity allows therefore a better selection of possible metals systems having good activity and selectivity.^[41,72–74] Examples of metal supports are gamma-alumina, zeolites, silica, ceria, and zirconia. The physicochemical nature of the catalyst is responsible for its stability; this includes its reduction behavior, vacant positions, polymorphic structure, crystallite size, lattice parameter and lattice strain (as a result of calcination temperatures), the elementary oxidation states and surface compositions, and the bonding of the support to metal cations.^[75] The most important feature in the field of catalysis is to produce high-performance catalysts increasing surface area and maintain its optimal pore volume and adjusted pore-size distribution.^[76] Along with the requirements of the catalyst and control parameters, the following five steps are needed to enable a heterogeneous reaction: (1) diffusion of reactants to the surface, (2) adsorption of reactants onto the surface, (3) reaction on the surface, (4) desorption of products off the surface, and (5) diffusion of products from the surface.^[23] The physicochemical nature of the catalyst is responsible for its activity.^[77–79] Temperature, reactants nature, formed products, the flow of reactant and products are factors that can affect the catalyst stability and make it change over time (also its selectivity).

2.3. General considerations about γ - Al_2O_3 as support

Many commercial catalysts consist of metal particles supported on high-surface-area oxide. Supports are the structural base of catalysts. Porosity and permeability of supports define their performance for mass transfer (which makes it possible for the reactions to occur).^[80] The most commonly used supports are silica and alumina.^[40] Alumina can exist in a variety of metastable structures, the so-called transition aluminas (such as X, κ , γ , δ , η , and θ) as well as its stable α - Al_2O_3 phase.^[81,82] Alumina polymorphism can be classified according to the oxygen sublattice structure and the distribution of aluminum ions in tetrahedral and octahedral interstitial sites. Thus, in α - Al_2O_3 , the oxygen sublattice is hexagonal-close-packed (hcp) structure with 2/3

of octahedral sites occupied with cations, while γ , δ , η , and θ have a face-centered cubic (fcc) arrangement of oxygen atoms and cations present in various proportions in both octahedral and tetrahedral sites.^[83] Sequential transformation throughout various transition alumina are formed before reaching the most stable α phase (this polymorphism is mainly a result of changes in the working conditions of pressure and temperature).^[44] Forms of hydrated alumina include trihydrate and monohydrate variants. The trihydrate is divided into gibbsite [γ -Al(OH)₃], bayerite (α -Al(OH)₃), doyleite, and nordstrandite, whereas the monohydrate form is divided into boehmite (γ -AlOOH), diaspore (α -AlOOH), and pseudoboehmite. Gibbsite is not only the main raw material source used to produce aluminum oxide by the widely known Bayer method in industry, but it is also the raw material to produce an important binder used in refractory castables.^[84,85] The sequence of transformations depends on the atmosphere (conditions of temperature, pressure, and medium, i.e. air or water vapor) and the grain size of the starting gibbsite, which yields products that possess certain surface conditions, shape, size of crystallites, pore size, and particle size for different applications.^[86,87] In air, fine-grained gibbsite is transformed to X, κ , or α -alumina, whereas coarse-grained gibbsite is transformed to boehmite and then to γ , δ , θ and-or α -alumina, depending on the temperature and especially in the presence of water vapor.^[88]

Two classes of aluminas are generally described, the low-surface-area α -alumina or corundum, and the highly porous aluminas, which are of catalytic interest (gamma-aluminas are perhaps the most common ones).^[89] Well-crystallized boehmite usually gives γ -Al₂O₃ with low surface area, whereas poorly crystallized boehmite, often called pseudoboehmite, gives the highest surface areas and is most frequently employed in catalysis.^[64] Transformation from γ -alumina to α -alumina is characterized by a decrease in surface area.^[51,90,91] Transition aluminas start to lose their surface area even below 800°C due to micropores elimination. Critical loss of surface area occurs above 1000°C with the eventual onset of crystallization to the thermodynamically stable alpha phase, confirming that catalytic properties of alumina largely depends on their crystalline structure and surface characteristics.^[5292-94] Gamma-aluminas are preferred because of their high surface area and relative stability below 900°C, and because they crystallize in a structure with a defective spinel structure γ -Al₂O₃ (gamma-alumina) as product of the dehydration of boehmite.^[95,96] In a spinel-like AB₂O₄ structure, cations A and B are replaced by aluminum (Al) leaving some vacant cation positions. Stoichiometric requirements imply that the spinel structure of γ -Al₂O₃ is described by the formula: (\square)Al₈O₁₂, where (\square) stands for a vacancy. Vacant positions have not yet been established, and the building of a theoretical direct reaction pathway connecting both reactant (AlOOH) and product (γ -Al₂O₃), is not possible.^[76] Despite the relevance of transition aluminas, their crystal structure is still being debated intensively, and their actual atomic-scale surface structure remains distinctly undetermined.^[97]

Gamma-alumina is widely used as a catalyst support material, usually used as pellets, with 190–200 m² g⁻¹ of surface area, pore volume: 0.55–0.70 cm³ g⁻¹, and mean pore diameter of about 8 nm.^[96,98–102]

2.4. γ -Al₂O₃–active-phase interactions

Aluminas have to be pretreated at elevated temperatures for the development of their catalytic activity. The weight loss corresponds to a steep decrease in the surface hydroxyl concentration; in parallel, the specific rate constant of conversion reaction greatly increases. This means that the removal of water and/or hydroxyl groups from alumina surface is essential for the development of catalytic characteristics. Gamma-alumina (γ -Al₂O₃) is a weak Brønsted acid and has a high number of Lewis acid sites. The density of surface hydroxyls ranges from 3 to 12 OH per nm² or from 10 to 15, depending on the author.^[97, 103] Coordinatively unsaturated (cus) anions (oxygen ions) and cations (exposed Al³⁺, anion vacancies) are created as a consequence of the removal of water and/or hydroxyl groups (surface ligands),^[103] and an anion vacancy (Lewis acid sites) is created which exposes a cus Al cation. This is the result of the regular dehydroxylation that can be described by the condensation of neighboring hydroxyls.^[76]

Acid and basic sites at the surface of γ -Al₂O₃ behave exactly as acid and basic substances in solution. Therefore, they respond reversibly to a change in the pH of the solution with the concomitant variation of the total surface charge, with the H⁺ and OH⁻ ions usually being regarded as potential determining ions (absence of specific adsorption). The surface charge of solid oxide is generally positive at low pH and negative at high pH.^[96] The hydroxyl groups which populate oxide surfaces become protonated (positively charged) or deprotonated (negatively charged) according to the pH value. The pH at which the surface is neutral is named the point of zero charge (PZC).^[104] At pH values lower or higher than the PZC, the surface is increasingly protonated or deprotonated, respectively. At the midrange PZC (7–9), alumina will adsorb anions at low pH and cations at high pH.^[40] The charge properties of gamma-alumina (as well as for any other oxide that acts like a support material) are reported in terms of PZC (as a function of surface ionization reactions). Along with surface ionization reactions, other parameters that fully characterize the charge properties of a particular oxide are hydroxyl group density (OH groups/area) and dielectric constant.^[105] Depending on the concentration of the type of sites, the oxides may show a tendency to adsorb cations (SiO₂, SiO₂-Al₂O₃, zeolites), anions (MgO, La₂O₃, ZnO), or both cations in basic solution and anions in acidic solution (Al₂O₃, TiO₂, Cr₂O₃).^[96]

Transition aluminas are frequently used as preshaped supports. These supported catalysts consist of an active metal oxide phase dispersed on an oxide support with high surface area.^[43] The chosen precursor is deposited onto the surface of the support via strong electrostatic adsorption. Once strongly adsorbed,

a pretreatment step is carried out (calcination or reduction), in such a way that the precursor is transformed into the active phase.^[40]

The final properties of the active phase depend mainly on the form in which the precursor is placed onto the support, and also on the nature and strength of precursor support interactions. In case of heterogeneous catalysts, the first step is the impregnation of the support. In this process, metal complexes are dissolved in aqueous solution and put in contact with a porous oxide (solid catalyst support). The most common methods for supported catalyst preparation make use of aqueous media by simple impregnation, or homogeneous deposition–precipitation, ion exchange, and specific adsorption. The choice of one or the other route is usually made by considering the nature and strength of the support–precursor interactions. During a certain contact time, the precursor adsorbs from an aqueous solution onto the support, and the catalyst is dried and further thermally pretreated. At this point, the precursor is transformed into the desired metal form (active form). Common subsequent steps are washing and drying, accompanied by catalyst activation (or irreversible transformation). So, final catalysts have well-dispersed active phase at nanometer scale, and are hydrothermally stable.^[96,105] Depending on the application, different metal profiles are required. For example, if selectivity loss due to consecutive side reactions is a concern, egg–shell catalysts, where most of the active components are deposited close to the particle surface, are advantageous since side reactions are suppressed. On the other hand, cases in which attrition causes a steady reduction in particle size, most of the active components should be deposited at the particle center (called egg–yolk profile). However, other applications might require uniform metal profiles. Different profiles can be obtained by controlled impregnation steps or by altering the starting compound.^[106]

The impregnation method is most commonly used and has been found to be more convenient not only to disperse the additives into the gamma-alumina for its stabilization by surface modification, but also for metal catalyst deposition. Impregnation is the procedure whereby a certain volume of solution containing the precursor of the active phase is in contact with the solid support. Two methods of contact may be distinguished, depending on the volume of solution: wet impregnation and incipient wetness impregnation. In wet impregnation, an excess of solution is used, and after a certain time the solid is separated and the excess solvent is removed by drying.^[107] In incipient wetness impregnation, the volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support. Control of the operation must be rather precise and repeated applications of the solution may be necessary. The incipient wetness method using water as suspending medium is usual for impregnation of the gamma-alumina with suitable additive precursors (for example, a copper salt) of appropriate concentration.^[94] It basically consists on imbibing a given amount of support in a volume of aqueous media corresponding to total volume of pores of the support. This amount is calculated on the basis of the support properties (as Brunauer, Emmet,

and Teller (BET) area, pore volume, and pore diameter), the amount of catalyst to prepare, and the final load of active phase that needs to be obtained. The impregnation solution is added dropwise to the support during intensive mixing. After addition of the solution, the support became slightly wet. This total volume of liquid is then just sufficient to fill the pores of the support until the so-called “incipient wetness point.” To generate the catalyst, the impregnated support is generally left to dry in air at an ambient temperature first, then dried at high temperature, and finally it is calcined. Examples of this procedure applied to the preparation of Au/TiO₂, Au/Ce_{0.62}Zr_{0.38}O₂ or Au/CZ, and Au/Al₂O₃ can be found in references,^[108–110] respectively. This technique is the simplest preparation procedure. Though this method might not result in the best dispersion of the active phase on the support, this process is preferred because it does not generate liquid waste due to its easy loading control.^[111] In addition, there were successful attempts to improve the metal dispersion using impregnation techniques to avoid its agglomeration on the support surface.^[109,112,113] The maximum loading is limited by the solubility of the precursor in the solution. In case of both methods the key operating variable is the temperature, which influences both the precursor solubility and the solution viscosity and, as a consequence, the wetting time. The concentration profile of the impregnated active phase depends on the mass transfer conditions within the pores during impregnation and drying.^[39]

Since metal loading is an important factor for the catalyst activity, studies have focused on the control of the metal profile in the support particle during impregnation.^[114,115] The choice of the optimal catalyst profile on the support is determined by the required activity, selectivity, and other characteristics of the chemical reaction (such as kinetics and mass transfer). The incorporation of metal phase only on the external surface of the pellet is recommended to avoid mass and heat transfer resistances into the center of the solid (“egg-shell” metal profile).^[116] When preparing an egg-shell type catalyst, the active phase is usually incorporated by the incipient wetness impregnation method, because it prevents long-range migration of the metal particles. Drying temperature and pH of the precursor solution might act as the key variables to control the migration of the metal particles (due to the metal-carrier interactions).^[117,118] The complete deposition of the intended amount of active phase on the γ -Al₂O₃ is the most important requisite for a proper preparation. The pH of the impregnation solution is a great matter of importance, in order to lead the generation of electrostatic forces and for the correct dispersion of the active phase.^[119] In general, the catalyst affects the chemical reaction throughout their active sites and their surface properties. Although the number of active sites increases by increasing metal loading, the dispersion of active phase will decrease with increasing loading.^[111] The degree of coverage of the catalytically active component also depends on the nature of the metal ions/complexes and the chemical species used in the impregnating solution. Those aspects greatly influence the resulting metal particle size and/or other characteristics of the finished catalyst.^[120] It is important to take this into account because it can lead to

reproducible synthesis routes, characterized by uniform distributions over support bodies of a highly dispersed active phase.^[121]

The effects of pH and ionic strength on catalyst distribution cannot be neglected.^[122] This pH dependence provides another degree of freedom in the engineering of the impregnation profiles, because adsorption of metal cations from aqueous solutions to various solid surfaces is strongly pH dependent. The adsorption of metal cations increases dramatically above a certain pH, but at a very low pH the metal cation to be adsorbed is usually in competition with the large excess of hydrogen ions. This effect has been attributed to the hydrolysis of the solid surface or the metal ion.^[120] In case of metals supported on gamma-alumina, the profile of the metal distribution within the pellet has been found to be very dependent on the conditions of impregnation, e.g. the adsorption of Co^{2+} , Ni^{2+} , or Zn^{2+} ammine complexes from aqueous solutions on $\gamma\text{-Al}_2\text{O}_3$. The adsorption isotherms exhibit a maximum for near-neutral impregnation pH ($6.5 < \text{pH} < 8.5$). Around this pH range, the formation of surface coprecipitates with Al^{3+} ions is verified. In case of impregnation of tungsten salts, alone or in combination with nickel or cobalt, the lack of adsorption of cobalt and nickel below pH 6 results from the inability of the positively charged metal ions to bind to the positive alumina surface, and above pH 8 metal hydroxides may precipitate. The reverse situation was observed for tungsten, since the metal ion adsorption increases as pH decreases. This reflects the negative charge of tungstate and polytungstate anions thus requiring alumina with a positive charge for adsorption onto their surface. In brief, adsorption is minimal at the PZC of alumina (between pH 8 and 9), and therefore this support should not be considered as inert during impregnation with metal ions in aqueous solutions, even under mild conditions (ambient temperature, working pH close to the PZC of the support and according contact times).^[99,123,124]

3. Characterization of solid catalyst

The surface characteristics and properties of solid support is a key issue in heterogeneous catalysis. Characterization of catalyst performance can be accomplished according to an integral study, throughout information about composition, structural features, surface morphology, adsorbate, electronic states, chemical reactivity, and local composition, among others.^[40,125] Some of the most used techniques in catalysis field for solids characterization are summarized in Table 2.

4. Measurement of contaminant degradation

Industrial wastewaters are very complex, principally due to the broad variety of compounds they may contain. The quantitative determination of all or even most organic compounds is not feasible, so the interest in using global indicators increases for both pollution and quality checking. In case of chemical characterization of wastewaters, there is a widespread use of two global referential parameters: Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD).^[153–155]

Table 2. Most used techniques for solids characterization in catalyst field.

Symbol	Technique	Property measured	Refs.
XRD	X-ray diffraction	Structure	[126–130]
SEM/TEM	Scanning electron microscopy/ transmission electron microscopy	Morphology/microstructure and species within the catalyst	[98, 131–134]
BET area TPR; TPD	Brunauer, Emmett, and Teller Temperature-programmed desorption and reaction:	Area/pore structure/pore volume Oxidation states	[73, 123, 135, 136] [78, 98, 128, 137]
TGA	Thermogravimetry and thermal analysis	Microscopic weight changes/ composition	[138, 139]
IR	Infrared spectroscopy	Adsorbate	[79, 140, 141]
RAMAN	Raman spectroscopy	Structure	[142–144]
XPS	X-ray photoelectron spectroscopy	Surface composition and oxidation states	[144–146]
FT-IR	Fourier transform infrared spectroscopy	Surface concentrations of active intermediates	[147, 148]
NMR	Nuclear magnetic resonance	Structure	[149, 150]
ESR/EPR	Electron spin resonance/electron paramagnetic resonance	Catalytic active sites or reaction intermediates with unpaired electrons	[151, 152]

TOC represents the total organic carbon present in the sample,^[156–159] whereas COD represents the oxygen required to chemically oxidize the organic matter in the sample. Moreover, recalcitrant COD represents the oxygen required to chemically oxidize the “non-biologically degradable” organic matter in the sample.^[28,160–162] Both parameters provide quantitative and qualitative information from the absolute value and the variation trend of organic matter in the effluent.^[163] Both are U.S. standard methods according to the American Public Health Association. A detailed discussion about the differences between the U.S. Environmental Protection Agency and the German Deutsche Industrie Norm COD protocols can be found in the study of Janicke (1983).^[153]

5. Classical Fenton system

The reaction of iron with hydrogen peroxide (developed by Henry John Horstman Fenton in the 1890s) has been extensively used to study the oxidation of a variety of organic compounds, as one of the main advanced treatment for recalcitrant compounds.^[17, 30, 164–168]

Classical Fenton consists of ferrous salts combined with hydrogen peroxide under acidic conditions to oxidize organic matter. This reaction allows the regeneration of hydroxyl radicals as shown in Fig. 1.^[169] The reaction mechanism has not been completely explained due to the variety of complex intermediate compounds which are formed, and their subsequent reactions.^[170]

Ferrous iron (Fe^{2+}) initiates the decomposition of H_2O_2 , and generates hydroxyl radicals (Fig. 1), involving a complex reaction sequence in an aqueous solution. However, the nonspecific and enhanced reactivity of $\text{HO}\bullet$ toward both organic and inorganic substrates result in various competitive processes that negatively affect the organic oxidation process. Fenton systems success is based on several reasons^[172]:

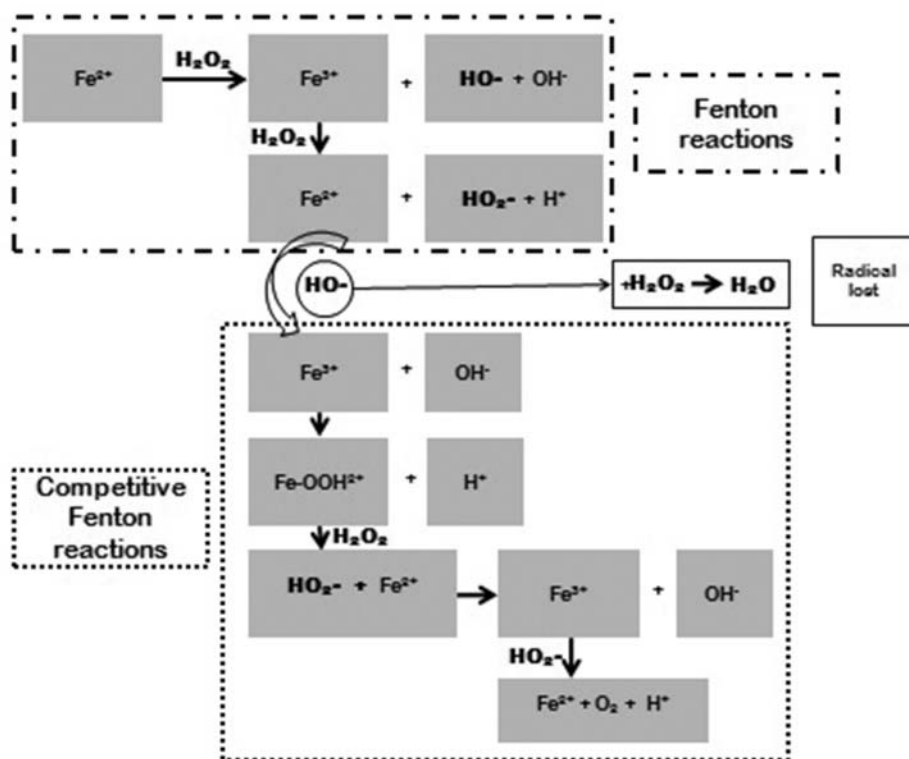


Figure 1. Fenton reactions in acidic pH (adapted from ^[14,171]).

- (1) Mild working conditions, such as ambient pressure and temperature, which avoids the requirement of complicated reactor facilities.
- (2) Simple and flexible, easy to implement either as unique treatment or integrated to an existing water treatment processes like coagulation, filtration, and biological oxidation.
- (3) Shortest reaction time of H_2O_2 activation and $\text{HO}\cdot$ generation among all other AOPs.
- (4) Cost-effective and practically viable, because of the use of cheap, moderately reactive, and easy-to-handle reagents (iron and H_2O_2).

In contrast, the main disadvantage of classical Fenton is that Fe^{2+} remains dissolved at neutral pH and Fe^{3+} disappears at $\text{pH} \geq 4$, forming ferric hydroxide sludge. As a consequence, acidic conditions ($\text{pH} < 4$) are needed for practical applications and neutralization is required before discharge, which is a huge economic drawback.^[41] To avoid this limitation, heterogeneous catalysts containing supported iron species (mostly Fe^{3+}) are used to generate $\text{HO}\cdot$. However, all iron-impregnated catalysts essentially contain Fe^{3+} , and the reaction between Fe^{3+} and H_2O_2 is at least three orders of magnitude slower than the classical Fenton reaction (Fig. 1), thereby requiring UV irradiation to accelerate the reductive generation of Fe^{2+} .^[172] Another disadvantage of these systems is the leaching of supported Fe species.^[136]

To avoid precipitates during reaction, a low concentration of Fe(III) relative to H_2O_2 can be used for the catalytic conversion of H_2O_2 into $\bullet\text{OH}$. This system is also typically used only under acidic pH conditions ($< \text{pH } 3$), but the use of chelating agents (such as ethylenediaminetetraacetic acid (EDTA), tetraamino macrocyclic ligands (TAML), and porphyrins) can extend the useful range of these Fe(III)/Fe(II) system to neutral pH conditions.^[173–176] Fe(II) and Fe(III) species are always present simultaneously (see Fig. 1), regardless of which species is used to initiate the reaction and so distinguishing between them might be useless, especially if a large molar excess of H_2O_2 is added. All Fe(II) is quickly oxidized to Fe(III) and thereafter the system will behave as independent of the initial oxidation state of iron.^[177,178] Zero-valent metallic iron in Fenton-type reactions has been also widely studied as an alternative to Fe(II) systems. Serving as an electron donor, it represents the most common metallic reducing agent used both supported onto an inert material or in homogeneous phase.^[179–182] Another possibility to overcome the disadvantages of Fenton process is the use of hybrid processes such as sono-Fenton, photo-Fenton, and electro-Fenton.^[177]

Cu(II) has been also tested as a possible alternative to solve the pH restriction ($\text{pH} < 4$) of Fenton reaction.^[183,184] Many industrial effluents exhibit pH values near neutrality, so working at near-neutral pH values is important for technical applications. The wide pH range of catalytic activity exhibited by copper catalyst may be advantageous for effluents with relatively high organic contents, since pH may vary along the treatment due to the formation of reaction intermediates.^[185] Copper-based systems, which have been used for the oxidation of diverse compounds, are listed in Table 3.

Catalyst reaction rate of bimetallic Cu/Fe is generally higher than that of monometallic Fe catalysts, which is attributed to the synergistic effect between the two redox couples, since the redox potential of each active phase (copper and iron) enhances the overall redox potential.^[204,205] Iron/Copper-based systems (and other bimetallic catalyst), which have been used for the oxidation of diverse compounds, are listed in Table 4.

6. Fenton-type system: Cu/ $\gamma\text{-Al}_2\text{O}_3$ catalysts

In some heterogeneous catalytic processes, CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts are regarded as promising candidates to solve the main drawbacks of working with iron-based systems, and also replacing high-cost metal-containing catalysts based on Pt. To face the rising environmental challenges, heterogeneous copper catalysts should offer higher activation efficiencies than the homogeneous Cu^{2+} ions, as well as good operational stability. The porous $\gamma\text{-Al}_2\text{O}_3$ plays an important role in the dispersion of CuO particles, in the minimization of copper ions leaching into the liquid phase, and also in the generation of Cu–OH complexes on the surface (which is the critical step for heterogeneous activation of H_2O_2 via a certain amount of basic surface sites on $\gamma\text{-Al}_2\text{O}_3$).^[220]

Various noble metals (Ru, Pt, Rh, Ir, and Pd) and some metal oxides (Cu, Mn, Co, Cr, V, Ti, Bi, and Zn) have traditionally been used as heterogeneous catalysts.

Table 3. Several copper-based systems which have been used in Fenton-type oxidation reactions.

Catalyst description	AOP	Treated material	Refs.
Copper-doped mesoporous silica microspheres (Cu-MSMs)	Fenton-type reaction	Phenytoin (PHT)	[186]
Copper sulfate (CuSO ₄)	Photo Fenton-type reaction	Diclofenac (DCF) and Carbamazepine (CBZ)	[187]
Copper oxide nanoparticles	Ultrasound Fenton-type reaction	Polycyclic aromatic hydrocarbons	[188]
Highly ordered mesoporous copper ferrite (meso-CuFe ₂ O ₄)	Fenton-type reaction	Imidacloprid (agricultural insecticide)	[189]
Cu (II) ions	Fenton-type reaction	Phenol	[190]
Copper-modified bentonite supported ferrioxalate catalyst (CuMBFOx)	Photo Fenton-type reaction	Direct Blue 71 (DB71), Acid Green 25 (AG25), and Reactive Blue 4 (RB4)	[191]
Copper oxide	Electro Fenton-type reaction	Cyanide	[192]
CuO.Fe ₂ O ₃	Fenton-type reaction	Bromophenol Blue, Chicago Sky Blue, Cu Phthalocyanine, Eosin Yellowish, Evans Blue, Naphthol Blue Black, Phenol Red, Poly B-411, Reactive Orange 16	[193]
Copper pyrovanadate	Photo Fenton-type reaction	Methylene blue (MB)	[194]
Cu (II) complexes	Photo Fenton-type reaction	Methyl Orange (MO)	[195]
Copper ions on bentonite	Photo Fenton-type reaction	Sunset Yellow FCF	[196]
CuSO ₄ .5H ₂ O	Fenton-type reaction	Thiocyanate	[197]
CuFeO ₂ microparticles	Fenton-type reaction	Bisphenol A	[198]
CuSO ₄	Fenton-type reaction	Phenol, benzoic acid, and methanol	[199]
CuFeZSM-5 zeolite	Fenton-type reaction	Azo dye Rhodamine 6G	[200]
Copper supported on aluminosilicate catalyst (Cu/MCM-41)	Photo Fenton-type reaction	Orange II	[201]
Copper supported on aluminosilicate catalyst (Cu/MCM-41)	Photo Fenton-type reaction	Phenol	[202]
Copper-impregnated pumice	Fenton-type reaction	Cyanide	[203]

Metal oxides are usually less active catalysts than noble metals. Nevertheless, metal oxides are more suitable to most applications since they are more resistant to poisoning. In addition, the combination of two or more metal oxide catalysts may improve catalytic activity and its nonselectivity.^[23] The order of reactivity of the supported metal ions is: $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Fe}^{3+} > \text{Ni}^{2+}$, and depends more strongly on the redox potential of metal ion, than on the supported amount. In the case of complexes (e.g. $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$) the more stable the complex, the greater its catalytic activity.^[221] To confirm the order of reactivity of supported metals, catalysts based on CuO, Fe₂O₃, NiO, and ZnO, supported on γ -Al₂O₃, have been prepared and tested in the treatment of chemimechanical pulping wastewaters using Fenton-type systems. Chemimechanical pulping combines chemical action prior to mechanical action. Wood chips are impregnated with sodium hydroxide and sodium sulfite (pH 9–10), and they are subsequently mechanically refined. Initial TOC of the effluent was 433 mg/L, directly measured from the diluted liquor. Possible compounds present in the liquor extracted by the alkaline sulfite treatment of mixed lignocellulosic biomass (willows, poplar, eucalyptus) are hydrolysable



Table 4. Several bimetallic systems which have been used in oxidation reactions.

Bimetallic catalyst	Treatment conditions	Treated material	Outcome	Refs.
Chitosan-Cu-Fe complex powders	0.05 g of catalyst, 25°C, 0.6 mL of H ₂ O ₂	100 mg L ⁻¹ of Reactive Black 5 (RB 5)	90% of dye removal	[206]
Al-Fe clays pillared	1 g of catalyst, 40°C, 36.27 mmol of H ₂ O ₂	2.76 mM of 4-chlorophenol (4-CP)	> 90% of 4-CP removal	[207]
Fe-Cu nanoclays	5.4%wt of Fe, 0.15 wt of Cu, 25°C	100 mL of Phenol	> 99% of 4-CP removal, 80% COD removal	[208]
Fe-Cu powder	0.154 mmol L ⁻¹ of Fe, 0.0078 mmol L ⁻¹ of Cu, 13.03 mmol L of H ₂ O ₂	3-nitroaniline (3-NA)	> 88% of 3-NA removal	[209]
Cu-doped Fe-pillared	0.8 g L ⁻¹ of catalyst, 25°C, 1000 mg L ⁻¹ of H ₂ O ₂ , UV radiation	150 mg L ⁻¹ of Phenol	> 99% Phenol removal	[210]
Micron-scale Fe-Cu	0.89 of g Cu/g Fe, 25°C	150 mL ⁻¹ of p-nitrophenol (PNP), 252 mg L ⁻¹ of TOC, 866 mg L ⁻¹ of COD	20% of TOC removal, 27% of COD removal	[211]
Au-Pd/ceria-zirconia	700 mg of catalyst, 60°C, PO ₂ of 3 bar	0.3 M of glycerol	> 90% of glycerol removal	[212]
Fe-Cu/MCM-41	0.2 g of catalyst, 14.4 mM of H ₂ O ₂	0.3 mM of Orange II	90% of TOC removal	[213]
Fe-Cu/MCM-41	0.2 g of catalyst, 14.4 mM of H ₂ O ₂ , 8 W UV-C	0.3 mM of Orange II	93% of TOC removal	[214]
Fe-Co/SBA-15	3.2 mM of catalyst, 20°C, ultrasonic power: 104.8 W/L	0.30 mM of Orange II	> 95% of discoloration	[215]
FeOx/NiOy/SBA-15	30 mg catalyst of catalyst, 300 μL of H ₂ O ₂	100 mg L ⁻¹ of Bisphenol A (BMA)	83.7% of TOC removal	[205]
Fe-Cu/MCM-41	0.6 g/L of catalyst, 25°C, 10 mM 300 μL of H ₂ O ₂	50 mg L ⁻¹ of Acid Red 73 (AR 73)	80% of AR 73 removal	[216]
Cu-ZnO/γ-Al ₂ O ₃	0.03 g of catalyst, 40°C, 0.049 mg L ⁻¹ of H ₂ O ₂	200 mg L ⁻¹ of Phenol	85% of TOC removal	[217]
Pd-Pt/γ-Al ₂ O ₃	140°C, 900 kPa	5 g L ⁻¹ of Phenol	80% Phenol removal	[218]
	1 wt.% of catalyst, 200°C, 2.3 MPa	1000 mg L ⁻¹ of dye mixture (Black 5, Blue 19, and Red 198)	44.1% of TOC removal for Black 5, 39.8% of TOC removal for Blue 19, and 46.8% of TOC removal for Red 198	[219]

tannins (polyphenols), condensed tannins, flavonoid-based, steroids (some of the steroids are esterified with fatty acids), and triterpenes. The catalysts based on Cu showed the best performance in terms of TOC reduction (52.7%) in contrast to catalyst based on Fe (the degree of mineralization was only about 30%).^[222]

Among all heterogeneous catalysts, those based on copper oxides show higher oxidation activities and are commonly used to study the catalytic oxidation of wastewater containing refractory pollutants.^[223] Reactivity of copper toward H_2O_2 is similar than that of iron at both oxidation states (Cu^+ and Cu^{2+}).^[172]

$\text{Cu}^{2+}/\text{H}_2\text{O}_2$ system can work over a broader pH range, compared to classical Fenton. Copper-based catalysts efficiently generate $\text{HO}\bullet$ in neutral or near-neutral aqueous solutions. Cu^{2+} complexes with organic degradation intermediates (generally organic acids) are easily decomposed by $\text{HO}\bullet$, and Cu^{2+} complexation does not deactivate the Fenton reaction, allowing the complete mineralization of organic pollutants. In brief, copper-based catalysts satisfy all basic redox criteria required to activate H_2O_2 in large-scale practical applications.^[172,224,225] For example, in case of aromatic hydroxylation at high pH, a decrease in activity was not observed for copper catalyst, while the inactivation of Fe at $\text{pH} > 8.5$ was demonstrated.^[226]

Several reaction mechanisms associated to copper in solution or on a solid catalyst have been presented.^[221,227] There are two possible pathways: a redox cyclic mechanism involving Cu^+ and Cu^{2+} , and the formation of the intermediate hydroperoxo complexes, which will subsequently generate hydroxyl radical. In this last case, Cu (II) complexes activate hydrogen peroxide for the oxidation of organic compounds, and the mechanism for peroxide activation involves the formation of a hydroperoxo complex, which then oxidizes the organic matter. The two pathways are characterized by a different turnover frequency as well as efficiency in H_2O_2 use. Starting from Cu^{2+} (as in Fenton-like heterogeneous catalysts), the occurrence of one or other pathway depends on the energetic stability of the hydroperoxo complex.^[31,228]

The possible and widely accepted mechanism of interaction between the H_2O_2 and the supported copper catalyst (Supp- Cu^{2+}) is shown in Fig. 2. The complex formed between supported copper and superoxide reacts with another H_2O_2 molecule to give the dioxygen, hydroxyl radical and water, and then the Supp- Cu^{2+} is regenerated by H_2O_2 , producing more $\text{HO}\bullet$ radicals.^[229]

Reaction between Supp- Cu^+ and H_2O_2 might be inhibited by molecular oxygen in acidic and near-neutral conditions, reducing the Cu^+ concentration needed to regenerate the Supp- Cu^{2+} through $\text{O}_2^{\bullet-}$ species.^[172] The effect of pH on the catalytic activity in copper-based systems can be explained by considering the pKa value of the acid-base equilibrium of $\bullet\text{O}_2\text{H}/\text{O}_2^{\bullet-}$ and the differences in the rate constant values associated with Cu (II)/ $\bullet\text{O}_2\text{H}$ and Cu (II)/ $\text{O}_2^{\bullet-}$ reactions. Therefore, as pH increases from 4 to 6, the fraction of $\text{O}_2^{\bullet-}$ substantially increases and the reduction of Cu(II) becomes faster, since $k_{\text{Cu (II)}/\text{O}_2^{\bullet-}} > k_{\text{Cu (II)}/\bullet\text{O}_2\text{H}}$. Beyond pH 7, the fraction of soluble Cu(II) significantly decreases, which becomes negligible at $\text{pH} > 8$.^[185] In homogeneous catalysts, fluxing the solution with N_2 reduces the amount of dissolved O_2 and improves the level of TOC reduction. In the heterogeneous case, however, $\text{O}_2^{\bullet-}$

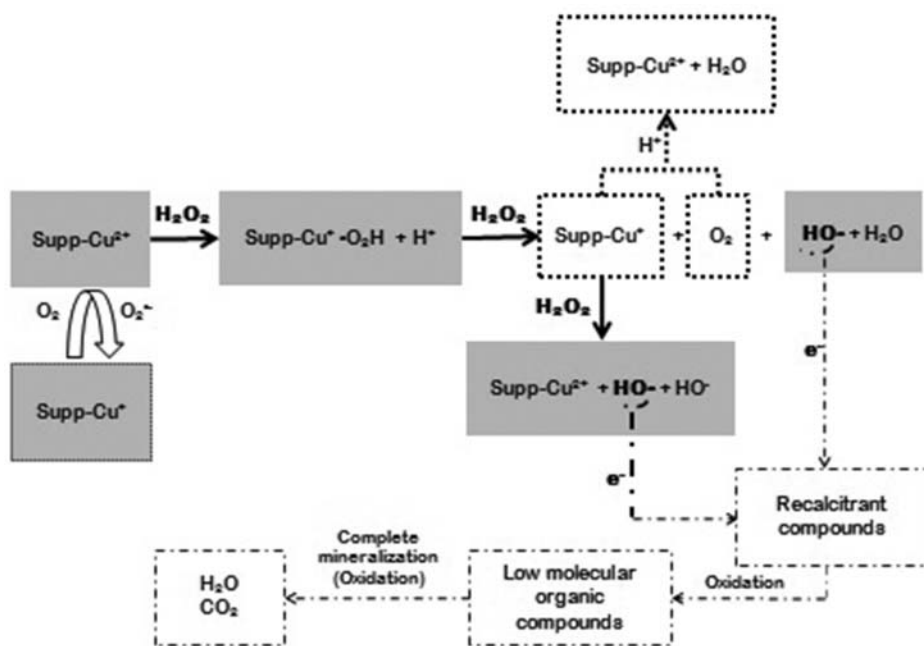


Figure 2. Proposed mechanism of interaction between the H_2O_2 and the supported copper catalyst (Supp-Cu^{2+}), (adapted from [229]).

species may also be generated from the chemisorption of dissolved oxygen on the catalyst, and from the reaction with electrons generated by the conversion of the organic species on the catalyst surface. These $\text{O}_2^{\bullet-}$ may react by introducing another pathway for the generation of Cu^+ species (Fig. 2). In other words, the dissolved oxygen mediates the reduction of Cu^{2+} to Cu^+ by electrons produced in the conversion of recalcitrant matter over the catalyst surface.^[31]

Studies performed on model compounds and different synthetic wastewaters have shown that metal loading and calcination of the precursor have great importance in determining the reduction degree of the catalysts, and, in turn, their activity during the oxidation reaction.^[127,230] To show the influence of calcination temperature and metal loading, copper/gamma-alumina precursors were prepared and calcined at different temperatures (from 500 to 900°C). The dispersion of the CuO phase onto the catalyst was evaluated using techniques such as BET surface areas, X-Ray Diffraction (XRD), Temperature-Programmed Reaction (TPR), and Scanning Electron Microscopy (SEM). Small differences could be observed in surface areas, pore diameter average, and pore volumes, between the different catalysts and also with respect to the supports. Good dispersions of the CuO phase were achieved even at higher calcination temperature (900°C). The samples showed a spinel-type phase demonstrating that copper aluminate was formed by the interaction of copper oxide with alumina. Free CuO was mainly obtained from the catalysts calcined at temperatures below 700°C, whereas copper aluminate was mostly obtained at temperatures over 700°C.^[231] Copper oxide is more active but less

stable in extreme conditions (e.g. hot acidic medium). On the other hand, spinel-type phase (such as copper aluminate) is more resistant to extreme conditions but is less catalytically active than “free” copper oxide.^[232] The nature of active copper species varies also with copper loading, i.e. isolated Cu^{2+} to bulk CuO. Copper catalysts with different loadings were characterized with TPR and XRD processes (all samples calcined at 500°C) to establish the chemical state of copper in the $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalysts. Characterization results showed isolated Cu^{2+} ions for 1 wt%; highly dispersed Cu^{2+} cluster for 5 and 7 wt%; and bulk CuO for 10–25 wt%.^[233] The catalysts exhibited significant differences in color depending on the amount of copper oxide loading. The catalysts samples with lower loadings showed in general bluish and greenish color (indicating the presence of isolated or dispersed copper ions), and black color for higher copper loadings (indicating the presence of bulk copper). Porosity properties of the catalysts as average pore diameters and pore volumes resulting from the impregnation are in agreement with high-porosity materials. Regardless of the nature of the phases inferred by the color of the samples, the porosity properties of the catalysts suggested good dispersion of the active component on the alumina support.^[135,221,233]

Copper-based catalysts have attracted more attention for their outstanding catalytic properties in a variety of catalytic reactions as shown in Table 5, being effective in the degradation and oxidation of organic recalcitrant matter.^[74,234–236]

Particularly, $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts have been widely used in environmental catalytic area. For example, spent liquor from a soda-sulfite chemimechanical pulping process (COD: 931 mg L^{-1} , and TOC: 433 mg L^{-1}) was treated with $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst resulting in 40–50% COD and TOC reductions, 80% of aromatic compounds reduction, and 90% of maximum discoloration.^[245] Copper supported on $\gamma\text{-Al}_2\text{O}_3$ has also been successfully applied for degradation of p-chlorophenol (200 mg L^{-1}); if combined with ultrasound, it provided higher p-chlorophenol and TOC removal with efficient H_2O_2 consumption.^[238] The highest TOC removal by phenol oxidation (200 mg L^{-1}) was 90% and it was 97% when combined with ultrasound. To explore the stability of the catalysts, Cu supported on alumina with loadings of 1, 5, 9, and 14 wt% were tested for phenol oxidation at 70°C in a cycle of five consecutive experiences. The samples containing 5, 9, and 14 wt% Cu(II) were found to remain stable and active after five experiments, and phenol removal achieved 95%. The results suggested that dispersed copper ions associated with low loading are more susceptible to deactivation due to the formation of large quantities of low molecular weight products (mainly acetic acid and p-benzoquinone, together with polymeric products).^[135] The $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ system was also used in effluents from the textile industry, which are characterized by very high COD and TOC as well as strong color because of the presence of azo group ($-\text{N}=\text{N}-$) associated with aromatic systems and auxochromes. Catalysts with various CuO loadings and those calcined at different temperatures were characterized by BET, SEM, XRD, and XPS. It was found that surface areas decreased with increasing CuO loadings, which can be expected if the pores of alumina are



Table 5. Copper-based systems supported on gamma-alumina for heterogeneous catalytic oxidation of recalcitrant organic compounds.

System	AOP	Treatment conditions	Treated material	Outcome	Refs.
9.55% wt of CuO/ γ -Al ₂ O ₃	Fenton-type reaction	0.20 g of catalyst, 21°C, 40 mM of H ₂ O ₂	100 mg L ⁻¹ of Black 5 (azo dye)	> 90% of dye removal	[237]
5.78% wt of CuO/ γ -Al ₂ O ₃	Electro Fenton-type reaction	70°C, H ₂ O ₂ in situ electrogenerated (VO ₂ :0.4 ml min ⁻¹ , Ec:-0.4 V)	80 mg L ⁻¹ of azo dye, 32 mg L ⁻¹ of TOC	90% of dye removal, 60% of TOC removal	[220]
g13% wt of CuO/ γ -Al ₂ O ₃	Fenton-type reaction	1 g of catalyst, 28°C, 24 mM of H ₂ O ₂	1.72 mM of 4-chlorophenol (4-CP)	71% of 4-CP removal	[25]
13% wt of CuO/ γ -Al ₂ O ₃	Ultrasound Fenton-type reaction	1 g L ⁻¹ of catalyst, 28°C, 1,600 mg L ⁻¹ of H ₂ O ₂ , power output of 100 W	200 mg L ⁻¹ of 4-chlorophenol (4-CP), 115 mg L ⁻¹ of TOC	98% of 4-CP removal, 70% of TOC removal	[238]
9% wt of CuO/ γ -Al ₂ O ₃	Microwave Fenton-type reaction	20 g L ⁻¹ of catalysts, 70°C, 15 mM of H ₂ O ₂	200 mg L ⁻¹ of phenol	97% of phenol removal, 90% of TOC removal	[135]
5% wt of CuO/ γ -Al ₂ O ₃ -MCM-41	Photo Fenton-type reaction	1 g L ⁻¹ of catalyst, UV, 25°C, 1.0 × 10 ⁻⁶ mol of H ₂ O ₂	100 mg L ⁻¹ of phenol, 2-chloro-4-nitrophenol, and 4-chloro-2-nitrophenol solution	> 99% of solution removal	[239]
0.70% wt of Cu/ γ -Al ₂ O ₃	Fenton-type reaction	33.6 mg L ⁻¹ of supported copper, 25°C, 0.05 M of H ₂ O ₂	0.025 mM of Methylene blue MB, (cationic dye)	18% of MB removal	[240]
5% wt of CuO/ γ -Al ₂ O ₃	Fenton-type reaction	1.5 g of catalyst, 70°C, 2.5 mL of H ₂ O ₂	632 mg L ⁻¹ of COD (of a dye mixture)	76.7% of COD removal	[241]
10% wt of CuO/ γ -Al ₂ O ₃	Microwave Fenton-type reaction	4 g L ⁻¹ of catalysts, 70°C, 15 mM of H ₂ O ₂ , microwave power: 100 W	50 mg L ⁻¹ of p-nitrophenol (PNP)	> 90% of PNP removal	[242]
6% wt of CuO/ γ -Al ₂ O ₃	Fenton-type reaction	1.5 g of catalyst, 10°C, 70 mM of H ₂ O ₂	10 mg L ⁻¹ of methyl tert-butyl ether (MTBE)	> 20% of MTBE removal	[243]
9% wt of CuO/ γ -Al ₂ O ₃	Microwave Fenton-type reaction	5 g L ⁻¹ of catalysts, 60°C, 15 mM of H ₂ O ₂ , microwave power: of 2450 MHz and 300 W	200 mg L ⁻¹ of 2-nitrophenol	97% of 2-nitrophenol and 79% of TOC removal	[244]

partially filled by CuO. The area also decreased with the increase in calcination temperature, indicating the apparent sintering of catalysts that negatively affects the activity during oxidation. The catalyst calcinated at 450°C, with Cu loading of 5.78 wt%, resulted to be the most efficient for activation of in situ electrogenerated H₂O₂, with 60% of TOC removal after reaction.^[220] In another study, catalytic discoloration of acid blue anionic azo 29 dye by H₂O₂ has been researched, and XRD tests were used to show intercalation of copper(II) complex into montmorilloniteK10 used as support. Discoloration efficiency was evaluated to ensure that catalyst crystallinity remained unchanged during the reaction of the dye with H₂O₂ (90% of the dye was decolorized in 33 min).^[246]

7. Conclusions

The main advantage of heterogeneous catalyst compared with homogeneous catalyst is the easiness of catalyst separation from the reaction medium, which represents a huge benefit from an economic point of view. Furthermore, it has a strong environmental benefit, because it avoids the accidental discharge of metal compounds into the receiving body.

The correct performance of the system based on γ -Al₂O₃ for the reduction or the elimination of refractory and/or toxic pollutants in wastewaters is determined by precision in the preparation methods of the support. This involves proper dispersion of active phase, good stability and activity of the catalyst, and adequate textural properties of the oxide.

The well-known iron-based systems for wastewater treatment have been widely studied, and a variety of alternatives are under investigation in order to solve the pH-limiting effect of iron species and other disadvantages. Copper-based catalysts emerged as very promising systems for more effective wastewater treatments. Their major advantage would be a broader pH operation range and a better resistance against catalyst deactivation processes. These catalysts could exhibit higher activity than iron-based materials during the oxidation reactions, with the concomitant higher reduction of hazardous compounds.

As summarized in the present work, the increasing interest in copper-containing systems has created a growing field of AOP applications. However, further research efforts should be done to accomplish a more comprehensive characterization of the chemical aspects of the processes. This might be critical to develop optimized features for both active species and support, and their potential synergistic interactions throughout the oxidation mechanism.

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