

New Fenton Catalysts

Subjects: Chemistry, Inorganic & Nuclear

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It is needed found Fenton catalysts with higher reaction rates with catalytic activity similar to the conventional catalysts. The spinel ferrites have attracted increasing interest due to their low cost, excellent catalytic activity, and magnetic properties that allow a facile separation and reutilization, in addition the presence of two different metals in an same structure can result in a better catalytic activity. Under the same idea the perovskites also result interesting for its use as Fenton catalysts due to the synergic effect between the metals of its structure.

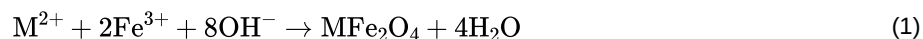
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1. Introduction

There are different methods of synthesis within which the following stand out:

- Chemical coprecipitation

Chemical coprecipitation is one of the most promising methods thanks to its ease of realization, as well as the possibility of mass production. It is mainly based on the co-precipitation of materials by a pH change. In general, this method consists of a mixture of precursors with the species of M^{2+} and M^{3+} (metal), to later precipitate the particles by the addition of a base (KOH, NaOH, or NH_4OH). It can be summarized in Equation (1) ^{[1][2][3][4]}.



2. Sol–Gel Method

This method is one of the most used for the synthesis of nanoparticles due to its relatively low cost, operational simplicity, and high homogeneity of the material obtained. It is based on a series of reactions, summarized in the hydrolysis of a metal alkoxide and the subsequent polycondensation of the hydroxyl groups formed, which produces a three-dimensional matrix^{[5][6][7]}, which must subsequently be subjected to thermal processes to improve the crystallinity of the nanoparticles.

3. Hydrothermal/Solvothermal

This process can be defined as a series of chemical reactions that occur in a closed system with one or more precursors in the presence of the solvent (water for the hydrothermal case), at a temperature above the boiling point of this^[8]. This process has several advantages such as its operational simplicity, versatility, and low cost, among others^{[9][10]}. An important advantage to highlight is the well-controlled diffusivity within the system^[11], which allows good control of the structure and morphology of the synthesized particles.

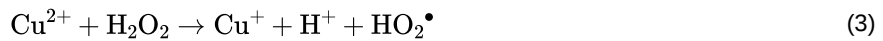
From these synthesis methods, it has been possible to obtain different new Fenton-type catalysts at the nanometer scale, with different coatings and supports^{[12][13][14]} in order to improve the efficiency of the hetero-Fenton process. It has been established that in the hetero-Fenton process, having a catalyst with a higher amount of transition-metal ions and a higher specific area leads to better Fenton activity^{[15][16]}. Fe_3O_4 is currently being extensively investigated as a Fenton catalyst^{[17][18][19]} due to its relatively high activity and easy magnetic separation. An essential advantage is the presence of Fe^{2+} and Fe^{3+} in a single material, due to its cubic structure where half of the Fe^{3+} ions occupied all of the tetrahedral sites and the Fe^{2+} ions are founded in the octahedral, allowing the presence of the two important species in Fenton processes. It has been reported in the literature that transition-metal ions occupying tetrahedral sites are catalytically inert, while those located at octahedral sites tend to determine catalytic activity, which is due to effect that the metal cations in these positions are found exclusively on the surface of the solid and thus take part in reactions to generate $OH^{\bullet}$ radicals ^[20]. It

has been suggested that the activation of H_2O_2 in the presence of magnetite takes place on the surface of the solid, i.e., the $\text{Fe}^{3+}\text{-OH}$ [21].

According to crystalline field theory, common metal cations have the following order of preference to occupy octahedral sites, $\text{Cr}^{3+} > \text{Ni}^{3+} > \text{Cu}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Fe}^{3+} > \text{Mn}^{2+} > \text{Zn}^{2+}$ [22]. The most studied are Fe, Mn, Cu, Ni, Zn, and Co[23][24].

Spinel ferrites have a general formula of $\text{A}^{2+}\text{B}^{3+}_2\text{O}^{-2}_4$ and a cubic lattice structure, where positions A and B are occupied by divalent and trivalent metal cations, according to the distribution of cations in the lattice, and the spinels can be normal, random, or inverse. In a normal spinel, tetrahedral sites are related to position A and octahedral sites to B. In a reverse spinel, tetrahedral sites are occupied by half of the B cations and the octahedral sites by all of the A cations. This distribution of cations is responsible for determining the magnetic properties of ferrites[25]. There are different types of spinel-structured materials; however, researchers will focus specifically on three of them: copper and cobalt ferrites and iron cobaltite.

Copper ferrite (CuFe_2O_4) is a well-known material with a reverse-spinel structure, which has a stable structure that reduces metals leaching, together with unique magnetic, electrical, physical, and chemical properties [26][27][28][29]. These properties make them a promising Fenton-type catalyst. Cu^+ ions have been reported to have the ability to generate $\text{OH}^\bullet$ radicals by a mechanism similar to that of Fe^{2+} according to Equations (2)–(4)[30].



Feng et al.[31] synthesized CuFe_2O_4 nanoparticles to be used as a Fenton catalyst in the degradation of sulfanilamide. They suggest that CuO is more reactive and effective than Fe^{3+} for the activation of H_2O_2 and, which is more important, can work in a higher pH range than conventional iron oxides. Moreover, Zhang et al.[32] observed that the leaching of Cu^{2+} is 30 times lower in CuFe_2O_4 than with CuO . The promising performance of the copper spinel ferrite as a Fenton catalyst was pointed out by several authors. Suraj et al. [33] synthesized CuFe_2O_4 by the chemical coprecipitation method and used it as a heterogeneous Fenton catalyst for the treatment of pulp and paper wastewater, obtaining a 78% elimination of the chemical oxygen demand. Ding et al. [34] demonstrated that the morphology of the spinel is also very important. They synthesized hollow CuFe_2O_4 spheres with oxygen vacancies (**Figure 1**), which demonstrated greater degradation of ciprofloxacin than normal CuFe_2O_4 particles. This better performance of hollow spheres was attributed, among other factors, to the synergistic oxygen vacancies and confinement effects on the catalyst surface. The oxygen vacancies produce highly active electron-rich Cu^+ species, which enhanced the H_2O_2 activation and, thus, the hydroxyl radical generation. In turn, the hollow structure is responsible for concentrating the organic pollutants near the $\text{OH}^\bullet$ -generator active sites, improving the organic pollutant molecules/ $\text{OH}^\bullet$ radicals contact, and accelerating the degradation. According to Yu et al. [35], the particle size and surface area are more important factors than a crystalline structure for improving the catalytic efficiency of CuFe_2O_4 . López-Ramón et al. [36] evaluated the effect of calcination temperature on the catalytic activity of CuFe_2O_4 synthesized by the sol–gel method, finding that the calcination temperature has two opposite effects: the activity decreases with increasing temperature due to the increase in crystalline size and cubic-to-tetragonal transformation of ferrite and appearance of hematite; however, the metal leaching decreases with increasing calcination temperatures.

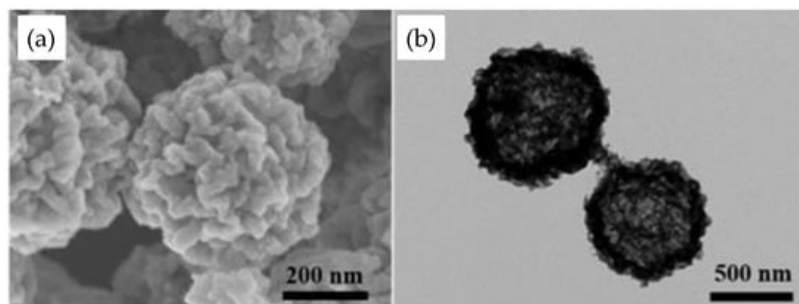
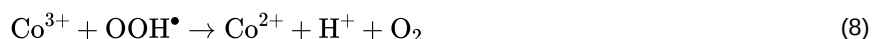


Figure 1. SEM (a) and TEM (b) of CuFe₂O₄ hollow spheres [34].

Cobalt ferrite (CoFe₂O₄), like other ferrites, has a high catalytic activity, stable crystal structure, low solubility, magnetic properties, as well as the ease of controlling the leaching of cobalt due to the strong interactions between metals, and the strong redox activity of Co with catalytic properties similar to those of noble metals (Pt, Ir, and Au) [37][38][39][40], which make it a promising material as a Fenton-like catalyst.

Feng et al. [41] synthesized monodispersed CoFe₂O₄ nanoparticles by a solvothermal method to evaluate them as a Fenton catalyst in the degradation of methylene blue, reaching a concentration decrease of 96.8%. The authors highlighted that the existence of Co²⁺ ions could favor the decomposition of H₂O₂ to OH[•] and subsequently give way to different reactions, as evidenced in Equations (5)–(8).



Sing and Singhal [42] demonstrated that the transition-metal doping of cobalt ferrites is a promising method for tuning the physical characteristics of catalysts and thus, enhancing their catalytic and magnetic properties. For that, the authors synthesized a series of Ru-doped cobalt ferrite nanoparticles by the sol–gel method for the photo-Fenton degradation of red Remazol textile dye, achieving a degradation of approximately 90% within 120 min. The mechanism proposed is based on the photocatalytic and Fenton character of the Ru-modified ferrite. An electron-hole pair is created by the irradiation of cobalt ferrite nanoparticles with visible light. The photogenerated electrons are responsible for the OH[•] generation from H₂O₂ and also the reduction of the Fe³⁺ cation on cobalt ferrite to Fe²⁺, which further generates OH[•] radicals in the reaction with hydrogen peroxide. Vinosha et al. [43] also analyzed the photo-Fenton performance of CoFe₂O₄ nanoparticles obtained by means of chemical coprecipitation, achieving almost total degradation of methylene blue (~99.3% in 75 min) under visible light irradiation. As an outstanding result, they proposed that the pH used in the synthesis was not an impact parameter that affected the morphology of the catalyst; however, it significantly affects the particle size (a more alkaline (pH > 9) medium, larger crystallite size). It has been proposed that the reactions that lead to the formation of CoFe₂O₄ by the chemical coprecipitation method in an aqueous medium, are those presented in Equations (9) and (10) [44].



In turn, Iron cobaltite (FeCo₂O₄) has been also studied in environmental remediation and energy storage, thanks to its electrical properties and electrochemical performance [45]. In the energy storage field, Mohamed et al. demonstrated that iron cobaltite nanorods show a better capacity and lower overpotential as the cathode of lithium–O₂ batteries than other metal cobaltites (Mn, Ni, and Zn) [46] because the FeCo₂O₄ surface has the highest number of electropositive Co³⁺ active sites that improve the oxygen adsorption and Fe²⁺ in the tetrahedral site that favors the release of electrons to reduce oxygen. Yadav et al. [47] demonstrated that iron cobaltites are also efficient for supercapacitive and photocatalytic applications due to the valence states of the Fe³⁺/Fe²⁺ and Co³⁺/Co²⁺ species, which are considered active catalytic sites. These nanoflake-like iron cobaltites present a capacitance as high as 1230 F g⁻¹ (5 mV s⁻¹) with a good rate capability and superior cycling stability and also show a good photocatalytic performance achieving up to 94.19% degradation of crystal violet dye under sunlight illumination. However, despite this, very little work has been carried out with reference to their evaluation as a Fenton-like catalyst [48][49]. Zhang et al. [48] synthesized nitrogen-containing carbon/FeCo₂O₄ composites and analyzed their performances as Fenton catalysts for the degradation of methylene blue obtaining almost 100% removal in 10 min without pH adjustment, which was attributed to the uniform distribution of bimetals and nitrogen doping, which ensured the exposure of sites with high catalytic activity. Zhao et al. [49] analyzed the behavior of FeCo₂O₄/g–C₃N₄ as a photo-Fenton catalyst in the degradation of rhodamine B (RhB), obtaining 98% degradation in 45

min, which was attributed to a synergetic interaction between photocatalytic and Fenton-like reactions and the effective separation of the photogenerated charges. Therefore, it is proposed that the use of iron cobaltite as a pristine catalyst (without doping or support) in the Fenton reaction may be promising for future applications.

In general, spinel ferrites turn out to be attractive materials for catalytic activities in Fenton processes, mainly because they manage to improve the generation reaction of Fe^{2+} and achieve a synergistic effect between metal ions with valences similar to those of iron involved in the process (M^{2+} , M^{3+} , M: Metal).

Perovskites are other types of materials with promising catalytic activity that can be synthesized by the abovementioned methods (Chemical coprecipitation, sol–gel, and hydro/solvothermal) [50][51][52][53]. Perovskites can be defined as a type of mixed oxide with different formulations, binary (ABO), ternary (AA'BO or ABB'O), and quaternary (AA'BB'O), where A and B are cations sites occupied by alkali metals, alkaline-earth metals or rare-earth metals and transition metals, respectively [54].

Some perovskites have been studied in different Fenton-type reactions, for example, Carrasco-Díaz et al. [55] removed paracetamol by Fenton reaction using $\text{LaCu}_{1-x}\text{M}_x\text{O}_3$ (M = Mn, Ti) as the catalyst and determined that the most active catalyst was the one that contained the highest amount of Cu^{2+} at the surface. Moreover, they found that the titanium and manganese species seem not to be responsible for the improvement of activity with respect to the sample LaCuO_3 . Li et al. [56] synthesized a $\text{Ca}_{1-x}\text{FeO}_{3-\delta}$ perovskite and determined that the A-site cation can distort the FeO_6 octahedra in the perovskite and regulate the oxygen vacancies (OV) concentration; in this way, an A-site cation deficient of $\text{Ca}_{0.9}\text{FeO}_{3-\delta}$ results in an improved H_2O_2 activation for the degradation of tetracycline by a Fenton-like process. Similarly, Xie et al. [57] found that the copper incorporation in LaCoO_3 perovskite improved the electro-Fenton activity due to the enhancement of redox activity and oxygen vacancies, but in this case, by the substitution of B-site elements, which synergistically promoted the activation of hydrogen peroxide to a hydroxyl radical ($\cdot\text{OH}$). On the other hand, Rusevova et al. [58] degraded phenol via heterogeneous Fenton-like reactions using iron-containing LaFeO_3 and BiFeO_3 perovskites, and made a comparison with data reported in the literature using, as a catalyst, nano-sized Fe(II, III) oxide particles, determining that the perovskites synthesized had a higher catalytic activity. Zhao et al. [59] determined that BiFeO_3 supported in carbon aerogel (BFO/CA) with a three-dimensional (3D) structure improves the catalytic activity and stability of BiFeO_3 , resulting in an interesting strategy for the development of advanced catalysts for its possible application in Fenton processes.

In summary, perovskites are materials similar to spinel ferrites, and the contribution of two different metal species (formation of OVs) can be of interest to the Fenton process.

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