

Novel active heterogeneous Fenton system based on $\text{Fe}_{3-x}\text{M}_x\text{O}_4$ (Fe, Co, Mn, Ni): The role of M^{2+} species on the reactivity towards H_2O_2 reactions

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Received 4 May 2005; received in revised form 10 August 2005; accepted 20 August 2005

Available online 18 November 2005

Abstract

In this work, the effect of incorporation of M^{2+} species, i.e. Co^{2+} , Mn^{2+} and Ni^{2+} , into the magnetite structure to increase the reactivity towards H_2O_2 reactions was investigated. The following magnetites $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$, $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ and the iron oxides Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ were prepared and characterized by Mössbauer spectroscopy, XRD, BET surface area, magnetization and chemical analyses. The obtained results showed that the M^{2+} species at the octahedral site in the magnetite strongly affects the reactivity towards H_2O_2 , i.e. (i) the peroxide decomposition to O_2 and (ii) the oxidation of organic molecules, such as the dye methylene blue and chlorobenzene in aqueous medium. Experiments with maghemite, $\gamma\text{-Fe}_2\text{O}_3$ and hematite, $\alpha\text{-Fe}_2\text{O}_3$, showed very low activities compared to Fe_3O_4 , suggesting that the presence of Fe^{2+} in the oxide plays an important role for the activation of H_2O_2 . The presence of Co or Mn in the magnetite structure produced a remarkable increase in the reactivity, whereas Ni inhibited the H_2O_2 reactions. The obtained results suggest a surface initiated reaction involving $\text{M}_{\text{surf}}^{2+}$ (Fe, Co or Mn), producing HO^\bullet radicals, which can lead to two competitive reactions, i.e. the decomposition of H_2O_2 or the oxidation of organics present in the aqueous medium. The unique effect of Co and Mn is discussed in terms of the thermodynamically favorable $\text{Co}_{\text{surf}}^{3+}$ and $\text{Mn}_{\text{surf}}^{3+}$ reduction by $\text{Fe}_{\text{magnetite}}^{2+}$ regenerating the active species M^{2+} .

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Keywords: Fenton; Iron oxides; Magnetite; Oxidation

1. Introduction

The Fenton reagent, a mixture of Fe^{2+} and H_2O_2 is one of the most active systems for the oxidation of organics in water [1–3]. This reactivity is due to the in situ generation of highly oxidative species, i.e. hydroxyl radicals, according to the process:



The Fenton reaction is a homogeneous process and requires stoichiometric amounts of Fe^{2+} and large quantities of acid, usually H_2SO_4 , to produce the optimum pH 3. After the process the

effluent must be neutralized with a base to be safely discharged. Upon neutralization significant amounts of sludge are formed, which is an important limitation of the process due to disposal problems. The spent acid, base and the formed sludge, are evident drawbacks of the Fenton process. The development of active heterogeneous systems to promote the Fenton chemistry which can operate at near neutral pH is of considerable interest since it could offer some advantages, such as no need of acid or base, no sludge generation and the possibility of recycling the promoter [4].

Several recent studies have investigated different iron containing solids for the Fenton reaction, such as $\gamma\text{-FeOOH}$ [5], $\alpha\text{-FeOOH}$ [6], Fe_2O_3 and $\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ [7,8], goethite [9–11], Fe(II) supported on zeólita, Al_2O_3 and SiO_2 [12,13] and $\text{Fe}^0/\text{Al}_2\text{O}_3$ [14]. It has been observed that depending on the

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conditions employed these materials can promote the oxidation of different organic compounds, such as aromatic and aliphatic acids, phenols, aromatic hydrocarbons, chlorocompounds and textile dyes with hydrogen peroxide. However, many of these systems showed low activities or strong iron leaching due to low pH, which resulted in the classical homogeneous Fenton mechanism.

An iron oxide, which has not been investigated in detail for application in heterogeneous Fenton system, is the inverse spinel Fe_3O_4 , magnetite [15–18]. This oxide has several features which make it very interesting in the Fenton reaction, such as (i) it contains Fe^{2+} which might play an important role for the initiation of the Fenton reaction according to the classical Haber–Weiss mechanism (Eq. (1)), (ii) the octahedral site in the magnetite structure can easily accommodate both Fe^{2+} and Fe^{3+} , allowing the Fe species to be reversibly oxidized and reduced while keeping the same structure and (iii) Fe ions in the magnetite structure can be substituted by several transition metals with varied redox properties which can be used to tune the catalytic properties of these materials. Moreover, magnetites are magnetic materials and can be easily separated from the reaction medium by a simple magnetic separation procedure. In a preliminary work [19] it has been observed that, in fact, M^{2+} species in the magnetite structure play an important role in the Fenton chemistry.

Herein, the remarkable effect of Co, Mn and Ni in the magnetite structure, i.e. $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ ($x = 0.21, 0.26$ and 0.53), $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ ($x = 0, 0.19, 0.38, 0.63$ and 0.75) and $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ ($x = 0, 0.10, 0.28$ and 0.54) to promote the Fenton chemistry has been investigated in detail. Surface and structural characterization of the magnetites, kinetic data and mechanistic considerations are presented.

2. Experimental

2.1. Oxides synthesis and characterization

All chemicals were high purity grade and were used as purchased. Magnetite Fe_3O_4 was prepared from FeCl_3 , NH_4OH and $\text{CH}_3\text{COONH}_4$ by co-precipitation of the precursor ferric hydroxyacetate followed by thermal treatment at 430°C under N_2 atmosphere. The substituted magnetites $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$, $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ were prepared as described above with the addition of the nitrate salts of the metals Ni, Co and Mn. After preparation all the magnetites were kept under N_2 atmosphere to avoid long-term oxidation by air. Maghemite, $\gamma\text{-Fe}_2\text{O}_3$, was prepared by oxidation of magnetite, Fe_3O_4 with air at 180°C for 3 h. Hematite, $\alpha\text{-Fe}_2\text{O}_3$, was also prepared by oxidation of magnetite, Fe_3O_4 with air at 600°C for 3 h.

The magnetites were characterized by Fe^{2+} solubilization and titration with dichromate and total Fe by atomic absorption (Carl Zeiss Jena AAS). The surface area was determined by the BET method using a 22 cycles N_2 adsorption/desorption in an Autosorb 1 Quantachrome instrument. The transmission Mössbauer spectroscopy and the Conversion Electron Mössbauer Spectroscopy (CEMS) experiments were carried out in a spectrometer CMTE model MA250 with a $^{57}\text{Co}/\text{Rh}$ source at room temperature using $\alpha\text{-Fe}$ as reference with a throwing

gas (95% helium and 5% methane), proportional counter and a ^{57}Co . The γ -ray was oriented perpendicular to the sample.

Magnetization measurements were carried out in a portable magnetometer with magnetic field of 0.3 T calibrated with Ni metal. The powder XRD data were obtained in a Rigaku model Geigerflex using $\text{Cu K}\alpha$ radiation scanning from 2 to 75° at a scan rate of 4°min^{-1} . Scanning electron microscopy (SEM) analyses were carried out in a Jeol JKA 8900RL.

2.2. Reactions

The hydrogen peroxide (Synth) decomposition study was carried out with 7 mL solution at $[\text{H}_2\text{O}_2]$ of 2.9 mol L^{-1} with 30 mg catalyst by measuring the formation of gaseous O_2 in a volumetric glass system. The oxidation of the organics (50 mg L^{-1}) methylene blue, hydroquinone, phenol solutions with H_2O_2 (0.3 mol L^{-1}) at pH 6.0 (natural pH of the H_2O_2 solution) were carried out with a total volume of 10 mL and 30 mg of the oxide catalyst. The reactions were monitored by UV–vis measurements. All the reactions were carried out under magnetic stirring in a recirculating temperature controlled bath kept at $25 \pm 1^\circ\text{C}$.

3. Results and discussion

3.1. Characterization of magnetites

The three series of magnetite $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$, $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ were characterized by chemical analyses, Mössbauer spectroscopy powder XRD and magnetization measurements.

Chemical compositions for these magnetites, obtained by chemical analyses (Table 1), have shown that the Fe^{2+} content decreases with the addition of Mn, Co and Ni, suggesting that these metals are replacing mainly Fe^{2+} .

Mössbauer characterization of the magnetites $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ (Fig. 1), $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ clearly showed that as Co, Mn and Ni are added to the magnetite the site B in the spectrum, which is related to the octahedral site in the magnetite structure, concomitantly decreases. On the other hand, the presence of Co, Mn and Ni does not affect significantly the site A in

Table 1
Magnetization measurements, lattice parameters and chemical analyses for the Mn, Co and Ni substituted magnetites

Sample (M_x)	σ ($\text{J kg}^{-1}\text{T}^{-1}$)	a_0 (Å)	Formula (from chemical analyses)
Fe_3O_4	87	8.396	$\text{Fe}_{2.11}^{3+}\text{Fe}_{0.83}^{2+}\square_{0.06}\text{O}_4$
$\text{Mn}_{0.21}$	72	8.339	$\text{Fe}_{2.04}^{3+}\text{Fe}_{0.73}^{2+}\text{Mn}_{0.21}^{2+}\square_{0.02}\text{O}_4$
$\text{Mn}_{0.26}$	60	8.419	$\text{Fe}_{2.14}^{3+}\text{Fe}_{0.53}^{2+}\text{Mn}_{0.26}^{2+}\square_{0.07}\text{O}_4$
$\text{Mn}_{0.53}$	62	8.421	$\text{Fe}_{2.14}^{3+}\text{Fe}_{0.26}^{2+}\text{Mn}_{0.53}^{2+}\square_{0.07}\text{O}_4$
$\text{Co}_{0.19}$	67	8.392	$\text{Fe}_{2.07}^{3+}\text{Fe}_{0.71}^{2+}\text{Co}_{0.19}^{2+}\square_{0.03}\text{O}_4$
$\text{Co}_{0.38}$	50	8.389	$\text{Fe}_{2.04}^{3+}\text{Fe}_{0.56}^{2+}\text{Co}_{0.38}^{2+}\square_{0.02}\text{O}_4$
$\text{Co}_{0.75}$	40	8.395	$\text{Fe}_{2.02}^{3+}\text{Fe}_{0.22}^{2+}\text{Co}_{0.75}^{2+}\square_{0.01}\text{O}_4$
$\text{Ni}_{0.10}$	77	8.389	$\text{Fe}_{2.08}^{3+}\text{Fe}_{0.77}^{2+}\text{Ni}_{0.10}^{2+}\square_{0.04}\text{O}_4$
$\text{Ni}_{0.28}$	70	8.376	$\text{Fe}_{2.05}^{3+}\text{Fe}_{0.64}^{2+}\text{Ni}_{0.28}^{2+}\square_{0.03}\text{O}_4$
$\text{Ni}_{0.54}$	66	8.369	$\text{Fe}_{2.03}^{3+}\text{Fe}_{0.41}^{2+}\text{Ni}_{0.054}^{2+}\square_{0.01}\text{O}_4$

\square , Oxygen vacancy.

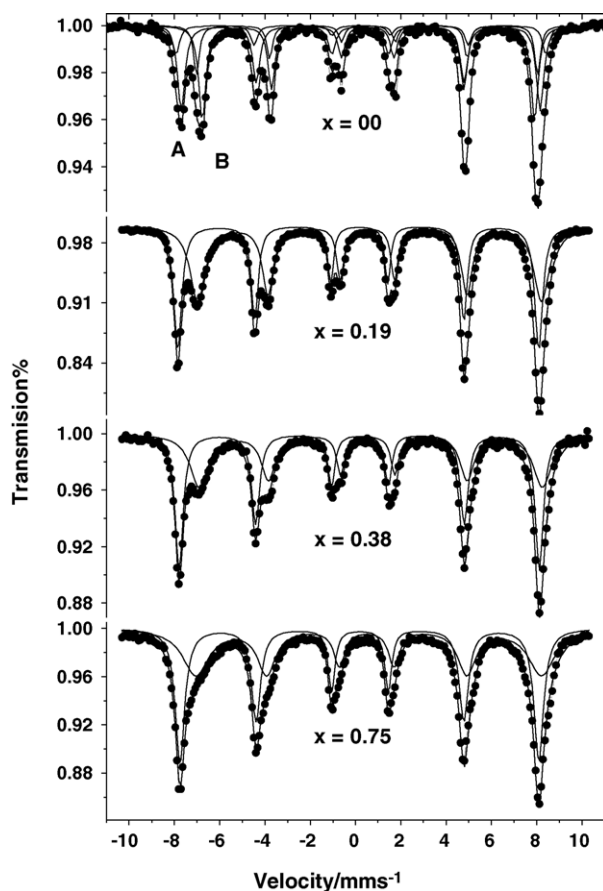


Fig. 1. Room temperature Mössbauer spectra of $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$.

the Mössbauer spectra of the magnetites. These results suggest that Co, Mn and Ni are replacing mainly Fe^{2+} at the octahedral site, i.e. $[\text{Fe}^{3+}]_{\text{tetrahedral}}[\text{Fe}^{3+}\text{Fe}_{1-x}^{2+}\text{M}_x^{2+}]_{\text{octahedral}}\text{O}_4$. The detailed discussion of the Mössbauer parameters obtained for these materials has been presented elsewhere [20,21].

The XRD patterns obtained suggested the presence of pure crystalline magnetite phases. A decrease in the lattice parameter from 8.396 Å for the pure magnetite to 8.392 and 8.389 Å for the Co series and to 8.389, 8.376 and 8.369 Å for the Ni series can be observed. On the other hand, due to its greater ionic radius, the increase in the Mn concentration in the magnetite produced an increase in the lattice parameters (Table 1). These results also support the incorporation of the metals Mn, Co and Ni into the oxide structure. As a result of these substitutions Co, Mn and Ni introduction, the magnetization measurements are strongly affected decreasing in all the cases (Table 1).

BET surface area measurements showed similar surface area of 14–16 $\text{m}^2 \text{g}^{-1}$ for all the oxides prepared. Also, no significant change was observed for the S_{BET} of the magnetite upon oxidation to $\gamma\text{-Fe}_2\text{O}_3$ at 180 °C and the transformation to $\alpha\text{-Fe}_2\text{O}_3$ at 600 °C.

3.2. Decomposition of H_2O_2 in the presence of iron oxides

The peroxide decomposition (Eq. (2)) was studied in the presence of different iron oxides $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), $\alpha\text{-Fe}_2\text{O}_3$

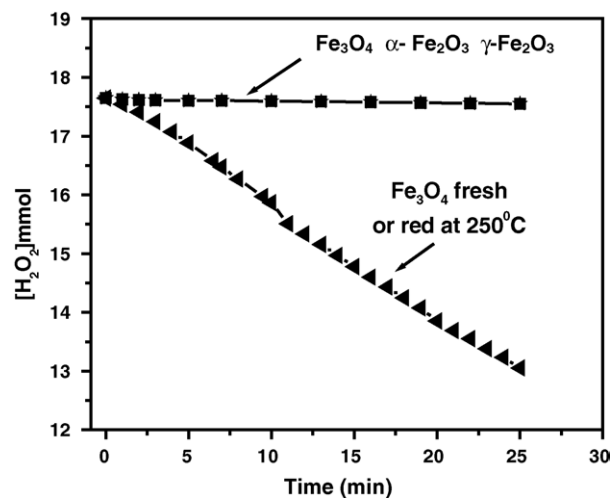


Fig. 2. Decomposition of H_2O_2 in presence of $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 exposed to air and Fe_3O_4 treated with H_2 at 250 °C for 1 h (28 °C, 30 mg, $[\text{H}_2\text{O}_2] = 2.9 \text{ mol L}^{-1}$, 7 mL).

(hematite), Fe_3O_4 and the series $\text{Fe}_{3-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Ni}$, Co and Mn).



Under the reaction conditions employed all the peroxide decomposition showed a zeroth order rate dependence on the H_2O_2 concentration, $V_{\text{dec}} = k_{\text{dec}}[\text{H}_2\text{O}_2]^0$. Very low activities were obtained for the decompositions carried out in the presence of the oxides containing only Fe^{3+} , i.e. $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and $\alpha\text{-Fe}_2\text{O}_3$ (hematite), with k rate constants of ca. $3 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$. On the other hand, freshly prepared magnetite showed a much higher H_2O_2 decomposition rate k of ca. $2 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ (Fig. 2). The same magnetite exposed to air for few weeks resulted in its surface 37% oxidized to maghemite, as revealed by CEMS, and a much lower activity with decomposition rate k of ca. $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$. If this air exposed magnetite was treated with H_2 at 250 °C for 60 min the oxidized phases present on its surface were completely reduced regenerating the Fe_3O_4 phase, as previously demonstrated by temperature programmed reduction studies [22]. After this reduction, the magnetite completely recovers its initial activity (Fig. 2).

These results clearly indicate that the presence of Fe^{2+} on the oxide surface should play an important role for the H_2O_2 activation.

3.3. The effect Co, Mn and Ni substitution on the H_2O_2 decomposition reaction

The H_2O_2 decomposition was also carried out in the presence of the series $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$, $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$, and the results are shown in Figs. 3–5, respectively.

We observed that the presence of Co and Mn into the magnetite structure strongly favored the peroxide decomposition. As the Co and Mn content increased in the magnetite the reaction rate also increased. On the other hand, the presence of nickel inhibited the reaction and as the Ni concen-

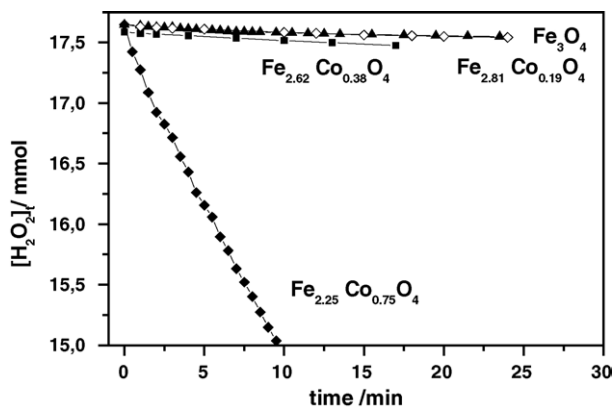


Fig. 3. Hydrogen peroxide decomposition in the presence of $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ (30 mg, $[\text{H}_2\text{O}_2] = 2.9 \text{ mol L}^{-1}$, 7 mL).

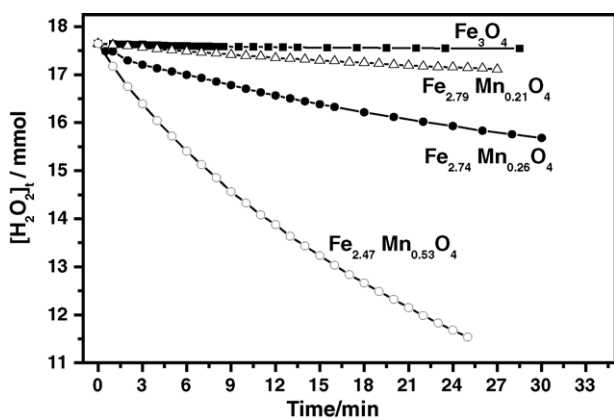


Fig. 4. Hydrogen peroxide decomposition in the presence of $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ (28 °C, 30 mg, $[\text{H}_2\text{O}_2] = 2.9 \text{ mol L}^{-1}$, 7 mL).

tration in the magnetite increased the reaction rate decreased (Fig. 5).

To investigate the possibility of homogeneous phase reactions promoted by Fe, Co or Mn species leached from the oxides it was carried out atomic absorption analyses of the remaining solution after 48 h reaction, which showed no significant

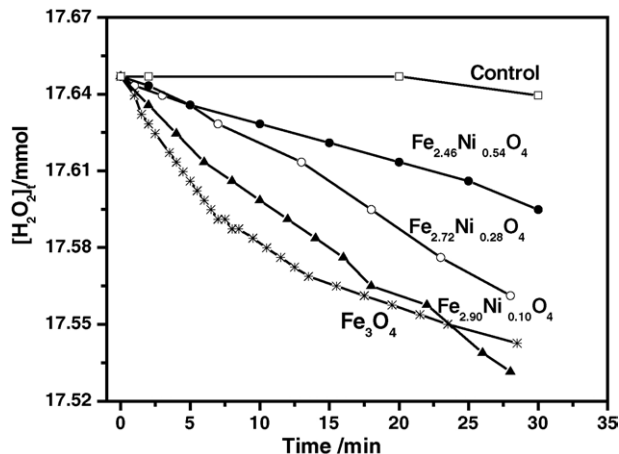


Fig. 5. Hydrogen peroxide decomposition in the presence of $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$ (28 °C, 30 mg, $[\text{H}_2\text{O}_2] = 2.9 \text{ mol L}^{-1}$, 7 mL).

metal concentration in solution. Moreover, two others experiments were carried out: (i) after the reactions in the presence of $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$, the solutions were filtered and the aqueous phase used for a second reaction and (ii) the magnetite was removed from the reaction medium during the reaction. The obtained results showed no significant activity in the absence of the magnetite, suggesting that the H_2O_2 decomposition is mainly heterogeneous taking place on the oxide surface and that the homogeneous reaction can be neglected.

The peroxide decomposition was also studied in the presence of the pure oxides Co_3O_4 and Fe_3O_4 . The obtained results showed that $\text{Fe}_{2.72}\text{Co}_{0.28}\text{O}_4$ is much more active with $k = 0.25 \text{ mmol min}^{-1}$ compared to the pure oxides, i.e. Co_3O_4 ($k = 0.039 \text{ mmol min}^{-1}$) and Fe_3O_4 ($k = 0.008 \text{ mmol min}^{-1}$). The homogeneous system CoCl_2 showed a relatively high decomposition rate constant $k = 0.15 \text{ mmol min}^{-1}$ which is likely related to the high concentration of $\text{Co}_{\text{aq}}^{2+}$. However, the heterogeneous system $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ was more active even compared to the homogenous CoCl_2 .

These results suggest that Co oxides or soluble cations alone are not responsible for the high activity observed by the substitute magnetites. Apparently, the combination of Fe with a second metal, e.g. Co or Mn, in the oxide structure is important to produce an active system.

3.4. Decomposition of H_2O_2 in the presence of organics

In order to investigate the occurrence of competitive reactions, the peroxide decomposition was also investigated in the presence of $\text{Fe}_{2.72}\text{Co}_{0.28}\text{O}_4$ and $\text{Fe}_{2.53}\text{Mn}_{0.47}\text{O}_4$ with the addition of different organics. The organic compounds added were phenol, hydroquinone, methylene blue and also the salt Na_2CO_3 , which are good radical scavengers [23–25]. The obtained results are displayed in Fig. 6.

It can be observed for the $\text{Fe}_{2.72}\text{Co}_{0.28}\text{O}_4$ that the presence of different organics or Na_2CO_3 led to a strong decrease in the H_2O_2 decomposition. It is interesting to note that hydroquinone, which is a very reactive molecule towards radicals, showed a

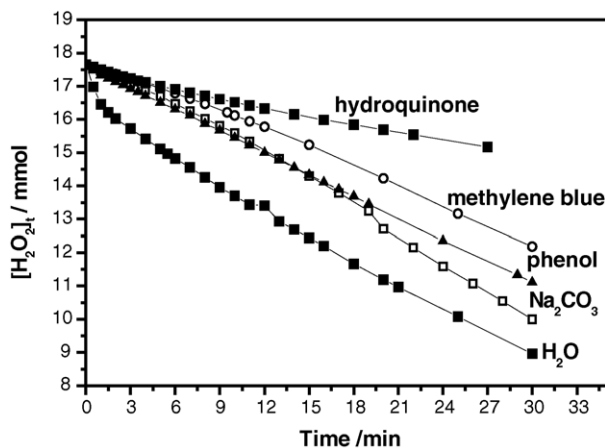


Fig. 6. Hydrogen peroxide decomposition in presence of $\text{Fe}_{2.72}\text{Co}_{0.28}\text{O}_4$ with the addition of phenol, hydroquinone, methylene blue and Na_2CO_3 (0.1 g L^{-1}) (28 °C, 30 mg, $[\text{H}_2\text{O}_2] = 2.9 \text{ mol L}^{-1}$, 7 mL).

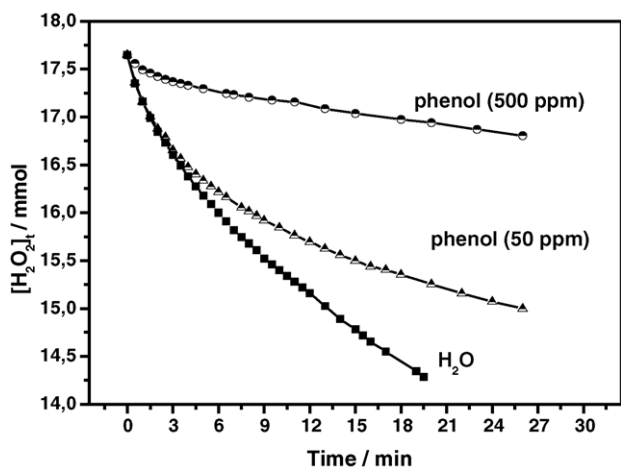


Fig. 7. Hydrogen peroxide decomposition in the presence of $\text{Fe}_{2.47}\text{Mn}_{0.53}\text{O}_4$ with different phenol concentrations (28°C , 30 mg, $[\text{H}_2\text{O}_2]=2.9\text{ mol L}^{-1}$, 7 mL).

more pronounced effect. Also, for the magnetite $\text{Fe}_{2.53}\text{Mn}_{0.47}\text{O}_4$ the presence of phenol and chlorobenzene caused a significant decrease in the H_2O_2 decomposition. Experiments with methylene blue dye at different concentrations showed that the peroxide decomposition was directly dependent on the organic concentration, decreasing from $k=0.256\text{ mmol min}^{-1}$ in the absence of methylene blue to $k=0.071\text{ mmol min}^{-1}$ in the reaction carried out in a 5 g L^{-1} solution of methylene blue. Also, the decomposition of H_2O_2 in the presence of phenol showed a strong inhibition effect as the phenol concentration increased to 50 and 500 ppm (Fig. 7).

3.5. Oxidation of organics by the system $\text{Fe}_{3-x}\text{M}_x\text{O}_4/\text{H}_2\text{O}_2$

To study the oxidation of organics by the system $\text{Fe}_{3-x}\text{M}_x\text{O}_4$ the dye methylene blue was selected as a probe molecule. The dye methylene blue show several advantages, such as: (i) it allows the use of simple spectrophotometric measurements at 633 nm to monitor the reaction and its kinetics and (ii) the cationic dye does not adsorb on the iron oxides surface since at the reaction pH (5.5–6.0) the oxides surfaces are positively charged according to their PZC (6.6 up to 8.0 for magnetite and maghemite and 6.7–10.0 for $\alpha\text{-Fe}_2\text{O}_3$) [24,25]. In fact, preliminary experiments with methylene blue solutions and different iron oxides, i.e. Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ showed that no adsorption takes place under the experimental conditions employed.

The discoloration plots obtained for the different oxides are shown in Fig. 8. Under the conditions employed no significant discoloration was produced by the Fe_2O_3 oxides. The results showed a low discoloration activity for Fe_3O_4 or $\text{Fe}_{2.54}\text{Ni}_{0.44}\text{O}_4$ with only 10% color reduction after 50 min. However, Mn and Co substituted magnetites showed very high oxidation activities with complete discoloration of the solution with 5 and 10 min, respectively. To calculate the discoloration rates, the decrease in absorbance in the first minutes of reaction was considered. The quasi-linear decrease in the absorbance was approximated to a pseudo zeroth order dependence of the discoloration rate

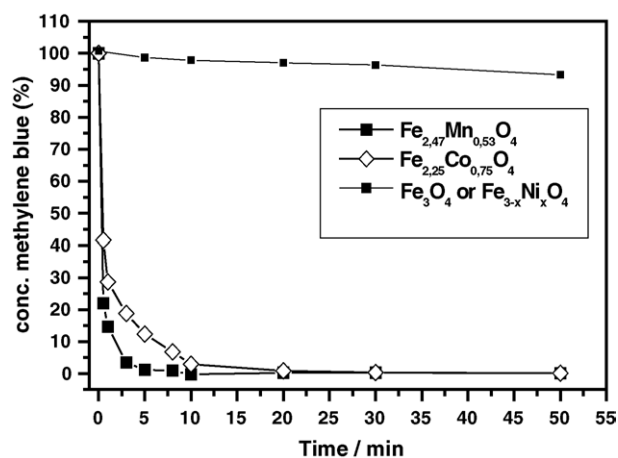


Fig. 8. Methylene blue (0.1 g L^{-1}) oxidation in the presence of H_2O_2 and $\text{Fe}_{3-x}\text{M}_x\text{O}_4$ ($\text{M}=\text{Co}$ and Mn) (30 mg, $[\text{H}_2\text{O}_2]=0.3\text{ mol L}^{-1}$, 10 mL).

on the dye concentration. Therefore, the obtained rate constants for magnetite with Co and Mn were 0.11 and $0.15\text{ g L}^{-1}\text{ min}^{-1}$, respectively.

The $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ magnetites were also studied for the H_2O_2 oxidation of chlorobenzene (0.03 g L^{-1}) in aqueous medium in a preliminary work using the membrane introduction mass spectrometry (MIMS) technique. This technique was used to investigate the mechanism of the oxidation of chlorobenzene by the classical homogeneous Fenton reagent showing the consecutive formation of the intermediates hydroquinone and quinone [26]. In these experiments, a 10 mL solution containing chlorobenzene at 0.02 g L^{-1} and H_2O_2 at 10.2 g L^{-1} (0.3 mol L^{-1}) was mixed with 30 mg of the different iron oxides and the chlorobenzene consumption was monitored by its mass spectrometric signal m/z 112. The results obtained showed that magnetites Fe_3O_4 , $\text{Fe}_{2.79}\text{Mn}_{0.21}\text{O}_4$, $\text{Fe}_{2.74}\text{Mn}_{0.26}\text{O}_4$ and $\text{Fe}_{2.47}\text{Mn}_{0.53}\text{O}_4$ converted 1, 5, 7 and 14%, respectively, of chlorobenzene after 30 min reaction (MIMS profile not shown). These results clearly indicate that the presence of Mn in the magnetite structure significantly increased the activity for the organic oxidation.

3.6. Mössbauer study of the magnetites used in the reaction

To study the effect of the H_2O_2 reaction on the different magnetites Mössbauer spectroscopy was used. Transmission Mössbauer spectra of the materials before and after 48 h reaction with H_2O_2 did not show any difference. It was also carried out surface Mössbauer spectroscopy CEMS of Fe_3O_4 before and after the reaction with H_2O_2 (Fig. 9). It is important to mention that exactly the same sample was used and the same set of adjusting parameters was applied to treat the Mössbauer data. The obtained Mössbauer results for Fe_3O_4 (Table 2) suggested the presence of three signals relative to the magnetite octahedral site A ($\text{Fe}^{2+}/\text{Fe}^{3+}$) and tetrahedral site B (Fe^{3+}) at 0.67 and 0.27 mm s^{-1} , respectively, and a Fe^{3+} signal at δ 0.32 mm s^{-1} , likely related to a surface oxidized magnetite. Upon reaction with H_2O_2 it can be observed that the magnetite site A signal slightly decreased from 41 to 39%,

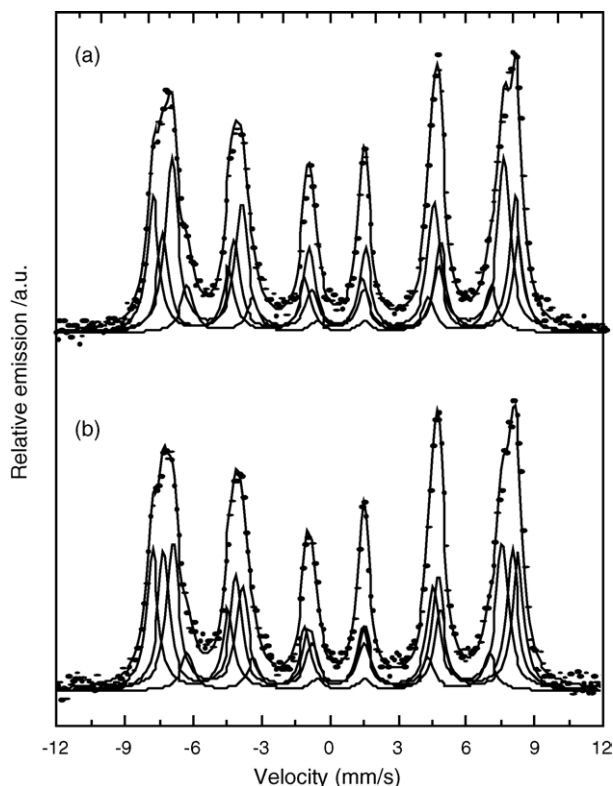


Fig. 9. Room temperature CEMS of Fe_3O_4 after (a), before (b) reaction with H_2O_2 (28°C , $[\text{H}_2\text{O}_2] = 2.9 \text{ mol L}^{-1}$ for 48 h).

whereas the relative intensity site B (Fe^{3+}) showed a slight increase from 22 to 25%. From these results it can be drawn that the A/B signal ratio of 1.86 decreases to 1.56 after the reaction. The same CEMS measurements were carried out for the magnetite $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ (data not presented) showing four signals, two signals for $\text{Fe}^{2+}/\text{Fe}^{3+}$ magnetite at $0.50\text{--}0.54$ and $0.44\text{--}0.45 \text{ mm s}^{-1}$, a Fe^{3+} magnetite $0.42\text{--}0.49 \text{ mm s}^{-1}$ and an oxidized magnetite Fe^{3+} signal at $0.25\text{--}0.30 \text{ mm s}^{-1}$. It can be observed that upon treatment with H_2O_2 the relative area for the signals related $\text{Fe}^{2+}/\text{Fe}^{3+}$ magnetite decreased from 47 to 40% after reaction with H_2O_2 , whereas the relative intensity for the signal for Fe^{3+} (at $0.25\text{--}0.30 \text{ mm s}^{-1}$) increased from 53 to 60%. Although CEMS detects a depth of approximately 3000 \AA and it is less sensitive to surface modifications, these results seem to suggest that an oxidation of the iron species might be taking place.

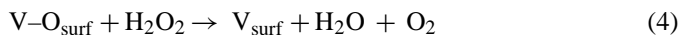
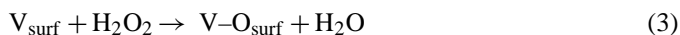
Table 2
Mössbauer hyperfine parameters at room temperature for Fe_3O_4 before and after reaction H_2O_2 (28°C , $[\text{H}_2\text{O}_2] = 2.9 \text{ mol L}^{-1}$ for 48 h)

	δ (mm s^{-1}) \pm (0.05)	ε (mm s^{-1}) \pm (0.05)	B_{hf} (T) \pm (0.06)	Relative area (%) \pm (1%)	A/B	Species
Fe_3O_4 (before)	0.67	0.06	46.9	(A) 41	1.86	$\text{Fe}^{2+}/\text{Fe}^{3+}$ magnetite Fe^{3+} magnetite Fe^{3+}
	0.27	-0.04	49.5	(B) 22		
	0.32	-0.01	50.6	37		
Fe_3O_4 (after)	0.69	0.07	46.9	(A) 39	1.56	$\text{Fe}^{2+}/\text{Fe}^{3+}$ magnetite Fe^{3+} magnetite Fe^{3+}
	0.27	-0.04	49.5	(B) 25		
	0.32	0.01	50.9	37		

δ , Isomer shift relative to $\alpha\text{-Fe}^0$; ε , quadrupole shift.

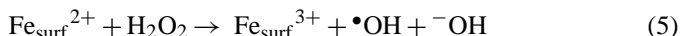
3.7. The reaction mechanism

The hydrogen peroxide decomposition promoted by transition metal oxide has been proposed in the literature to take place by two possible reaction pathways: (i) via a surface oxygen vacancies (V_{surf}) mechanism and (ii) via radical reactions. In the first mechanism, oxygen vacancies on the oxide surface participate in the reaction by activating H_2O_2 molecules to produce O_2 . A simplified view of this mechanism is given in Eqs. (3) and (4):

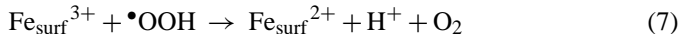


This mechanism has been proposed for different oxides, such as perovskites [27].

The formation of radicals from H_2O_2 and iron oxides has been proposed in the literature [28]. Although, the mechanism of radical generation is not clear, a simple proposal is the initiation by the reaction of H_2O_2 with partially reduced surface species, for example, Fe^{2+} , according to the Haber–Weiss mechanism:



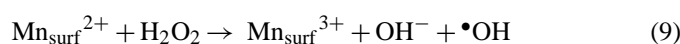
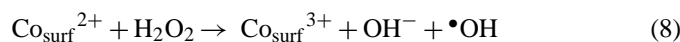
The formation of O_2 in a radical reaction can be very complex but a simple pathway can be proposed via the hydroperoxide radical:



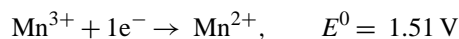
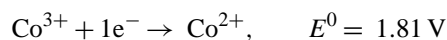
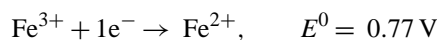
In these reactions a hydroperoxide radical intermediate is generated, which can then react with a surface species to produce O_2 and H^+ . The H^+ is then neutralized by the OH^- generated in Eq. (5).

The results presented in this work showed that the peroxide decomposition is strongly inhibited by the presence of organic compounds, especially radical scavengers, such as hydroquinone and Na_2CO_3 . These results suggest the occurrence of a radical mechanism. Once formed the radicals $\bullet\text{OH}$ or $\bullet\text{OOH}$ might react by two competitive reactions: pathway 1: the H_2O_2 decomposition and pathway 2: the organic oxidation. In fact, electrospray analyses of the reactions of phenol, aniline and chlorobenzene with H_2O_2 in the presence of Fe_3O_4 and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ have shown the formation of several hydroxylated intermediates, which strongly supports the participation of hydroxyl radicals in the reaction [29].

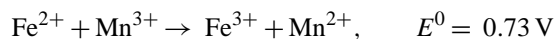
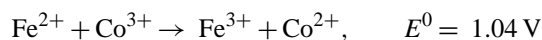
The presence of Mn and Co in the magnetite structure produced a remarkable increase in the peroxide decomposition and methylene blue oxidation. On the other hand, the presence of Ni inhibited both reactions. Although, the effect of these metals is not clear, several points can be raised in order to discuss their role in the reaction. For nickel it can be considered that only the Ni^{2+} species are stable and for this reason they cannot initiate the radical reaction according to Eq. (5). As Ni^{2+} replaces mainly Fe^{2+} in the magnetite structure, the reaction is inhibited since Fe^{2+} would be responsible for the initial step. On the other hand, cobalt and manganese exhibit the redox pairs $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$, which could also produce radicals according to the reactions:



However, as Co^{2+} and Mn^{2+} are replacing mainly Fe^{2+} , as indicated by the characterization data, the processes shown in Eqs. (8) and (9), would not be solely responsible for the remarkable increase in the activity exhibited by the substituted magnetites $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$. To explain the strong effect of Co and Mn substitution it could also be considered an electron transfer during the reaction. For example, based on the standard reduction potentials for the metals:



It can be considered that the reduction of Co^{3+} or Mn^{3+} by Fe^{2+} is thermodynamically favorable as shown by the following equations:



Therefore, one can envisage that Fe^{2+} in the oxide could reduce the Co^{3+} and Mn^{3+} surface species. This reduction could take place by an electron transfer process within the semiconductor oxide structure. Magnetite, Fe_3O_4 , is a semiconductor with a narrow band gap (0.1 eV) and shows a very high conductivity with almost metallic character (ca. 10^2 – $10^3 \Omega^{-1} \text{cm}^{-1}$) [30], which is important for electron transport.

The efficient regeneration of the surface Co^{2+} or Mn^{2+} species by this process would be responsible for the remarkable increase in activity of H_2O_2 decomposition and organic oxidation observed for these materials. If $\text{Fe}_{\text{magnetite}}^{3+}$ can be reduced during the decomposition of hydrogen peroxide (as shown in Eq. (7)) there is the possibility to regenerate the Fe^{2+} , which can make the process catalytic. However, more detailed studies are necessary to further investigate this proposed mechanism.

4. Conclusion

The results presented in this work showed that iron oxides could promote two reactions involving hydrogen peroxide: the decomposition to O_2 and the oxidation of organic compounds in aqueous medium. The introduction of Mn and Co to produce $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ and $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ resulted in a remarkable increase in the activity for both reactions, whereas the presence of Ni led to an inhibition of the process. The reaction apparently takes place via radical species, which can be generated by Fe^{2+} , Co^{2+} and Mn^{2+} . The high activity has been discussed in terms of thermodynamically favorable reduction of Co^{3+} and Mn^{3+} by Fe^{2+} by an electron transfer within the semiconductor oxide. These results are relevant for the understanding of the factors controlling the activation of H_2O_2 and radical generation on metal oxides surfaces. The studied systems showed potential for the development of advanced oxidation processes based on a heterogeneous Fenton system.

Acknowledgements

The authors wish to thank CAPES, CNPq, FAPEMIG and PRPq/UFMG.

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