

## Investigation of the Solid State Reaction of $\text{LaMnO}_3$ with $\text{Fe}^0$ and its effect on the Catalytic Reactions with $\text{H}_2\text{O}_2$

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Neste trabalho, reações entre a perovskita  $\text{LaMnO}_{3,15}$  e  $\text{Fe}^0$  foram promovidas pelo tratamento térmico da mistura  $\text{Fe}^0/\text{LaMnO}_{3,15}$  a 200, 400 e 600 °C. Análises por espectroscopia Mössbauer, difração de raios X (DRX), redução em temperatura programada (TPR) e desorção em temperatura programada ( $\text{O}_2$ -TPD) sugerem que a 400 °C e a 600 °C a perovskita transfere oxigênios para o  $\text{Fe}^0$ , produzindo uma perovskita deficiente em oxigênio,  $\text{LaMnO}_{3-\delta}$ , e formando óxidos de ferro altamente dispersos, principalmente  $\text{Fe}_3\text{O}_4$  e  $\text{FeO}$ . Os parâmetros de rede e os tamanhos de cristalitos obtidos por DRX mostram que o  $\text{LaMnO}_3$  sofre uma forte distorção da rede cristalina após a reação, mas sem o colapso da estrutura perovskita. Estudos de reatividade sugerem um efeito especial de interface na mistura  $\text{Fe}^0/\text{LaMnO}_3$  em duas reações com  $\text{H}_2\text{O}_2$ , *i.e.* a decomposição para produzir  $\text{O}_2$  e a oxidação da molécula modelo, o corante azul de metileno. Com o tratamento da mistura  $\text{Fe}^0/\text{LaMnO}_{3,15}$  a temperaturas mais altas, observa-se uma diminuição da atividade de decomposição do  $\text{H}_2\text{O}_2$ , porém um aumento na atividade de oxidação do corante. Estes resultados são discutidos em termos de uma diminuição da concentração das espécies  $\text{Mn}^{3+}_{\text{surf}}$  e  $\text{Mn}^{4+}_{\text{surf}}$ , ativas para a decomposição do  $\text{H}_2\text{O}_2$ , com a formação de espécies  $\text{Mn}^{2+}_{\text{surf}}$  e  $\text{Fe}^{2+}_{\text{surf}}$ , ativas para a reação de Fenton.

In this work, the reaction of the perovskite  $\text{LaMnO}_{3,15}$  with  $\text{Fe}^0$  has been promoted by thermal treatment of the mixture  $\text{Fe}^0/\text{LaMnO}_{3,15}$  at 200, 400 and 600 °C. Mössbauer spectroscopy, X-ray diffraction (XRD), temperature programmed reduction (TPR) and temperature programmed desorption ( $\text{O}_2$ -TPD) analyses suggested that at 400 and 600 °C oxygen from perovskite is transferred to  $\text{Fe}^0$  to produce an oxygen deficient perovskite,  $\text{LaMnO}_{3-\delta}$ , and highly dispersed iron oxides, mainly  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$ . XRD lattice parameters and crystallite size showed that  $\text{LaMnO}_3$  suffers a strong lattice distortion after reaction but no collapse of the perovskite structure. Reactivity studies pointed to a special interface effect of  $\text{Fe}^0/\text{LaMO}_3$  towards two reactions with  $\text{H}_2\text{O}_2$ , the decomposition to  $\text{O}_2$  and the oxidation of the model molecule, the methylene blue dye. As the treatment temperature of the  $\text{Fe}^0/\text{LaMnO}_{3,15}$  increased, the activity for  $\text{H}_2\text{O}_2$  decomposition decreased, whereas the activity for the dye oxidation increased. These results are discussed in terms of a decrease in the concentration of  $\text{Mn}^{4+}_{\text{surf}}$  and  $\text{Mn}^{3+}_{\text{surf}}$  species, active for the  $\text{H}_2\text{O}_2$  decomposition, with the formation of  $\text{Mn}^{2+}_{\text{surf}}$  and  $\text{Fe}^{2+}_{\text{surf}}$  species, active for the Fenton reaction.

**Keywords:** perovskites, iron oxides, Fenton, Mössbauer spectroscopy

### Introduction

Metallic iron and iron oxides have been extensively investigated in several environmental applications, such as the reductive treatment of organic and inorganic groundwater contaminants, e.g. reactive permeable

barriers,<sup>1,2</sup> and the advanced oxidation Fenton process.<sup>3-5</sup> This is mainly due to the versatile chemical-redox behavior, low toxicity and low cost of iron and iron oxides. However, these iron compounds show relatively low activity and many efforts in this area are currently directed to improve the efficiency and widen the application of these systems in environmental remediation processes.

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We have recently reported two ways to increase the activity of Fe<sup>0</sup> and iron oxides in these applications, *i.e.* (i) the combination of the oxide with metallic iron<sup>4,5</sup> and (ii) the introduction of Mn in the iron oxide structure.<sup>3,6</sup> The combination of Fe<sub>3</sub>O<sub>4</sub> with Fe<sup>0</sup> strongly increases the activity for the Fenton chemistry and also for the electron transfer reactions of Fe<sup>0</sup>.<sup>4,5</sup> This increase in activity was discussed in terms of a thermodynamically favorable electron transfer from Fe<sup>0</sup> to Fe<sub>3</sub>O<sub>4</sub> to generate Fe<sup>2+</sup><sub>surf</sub> species active for the reactions. Also, the presence of Mn in the oxide structure, e.g. Fe<sub>3-x</sub>Mn<sub>x</sub>O<sub>4</sub>, produces a remarkable increase in the activity for the Fenton reaction.<sup>3,6</sup> The high reactivity was explained by a redox cycle where Mn<sup>2+</sup><sub>surf</sub> species were oxidized by H<sub>2</sub>O<sub>2</sub> to generate radicals and subsequently regenerated by reduction of Mn<sup>3+</sup><sub>surf</sub> by Fe<sup>2+</sup><sub>bulk</sub>.

In this work, we investigate for the first time the use of the perovskite LaMnO<sub>3</sub> and the mixture Fe<sup>0</sup>/LaMnO<sub>3</sub> as catalysts in the Fenton reaction. The perovskites LaMnO<sub>3</sub> and its derivatives La<sub>1-x</sub>A<sub>x</sub>Mn<sub>1-y</sub>M<sub>y</sub>O<sub>3</sub> (where A can be a lanthanide, actinide, alkaline or earth alkaline metal and M a transition metal such as Co, Fe and Ni) show interesting properties for the reactions with H<sub>2</sub>O<sub>2</sub>, such as the possibility of Mn in different oxidation states, Mn<sup>2+</sup>, Mn<sup>3+</sup>, Mn<sup>4+</sup>, and a flexible oxygen stoichiometry (δ), allowing a control of their redox behavior.<sup>7</sup> Hereon, we describe in detail the interface reaction of LaMnO<sub>3</sub> with Fe<sup>0</sup> and its effect on the reactions with H<sub>2</sub>O<sub>2</sub>, *i.e.*, the decomposition to O<sub>2</sub> and the oxidation of the organic probe molecule, the methylene blue dye.

## Experimental

The perovskite LaMnO<sub>3</sub> was prepared by coprecipitation of a solution (85 mL) of Mn<sup>3+</sup><sub>aq</sub> 0.05 mol L<sup>-1</sup> (Mn(NO<sub>3</sub>)<sub>3</sub>, Synth) and La<sup>3+</sup><sub>aq</sub> 0.05 mol L<sup>-1</sup> (La(NO<sub>3</sub>)<sub>3</sub>, Synth) with NaOH (180 mL of 2 mol L<sup>-1</sup>) at room temperature. The solid obtained was extensively washed, dried at 80 °C for 5 h and treated at 800 °C in air for 4 h. The mixtures Fe<sup>0</sup>/LaMnO<sub>3</sub> used iron metal α-Fe<sup>0</sup> (Sicalab).

The Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures were prepared with a metal:oxide weight ratio of 1:1 by simple manual grinding for 60 s using an agate mortar. The thermal treatment was carried out in a quartz tube under argon (99.995%) flow (50 mL min<sup>-1</sup>) heated from room temperature to 200, 400 or 600 °C at 10 °C min<sup>-1</sup> and kept at the final temperature for 2 h. The mixtures were then quenched to room temperature under argon atmosphere by removing the quartz tube from the oven and using compressed air to cool down the external tube wall.

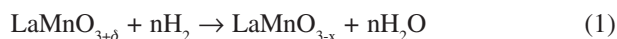
The transmission <sup>57</sup>Fe Mössbauer spectroscopy analysis was carried out on a CMTE spectrometer model MA250 with a <sup>57</sup>Co/Rh source at room temperature using α-Fe<sup>0</sup> as reference. Assuming that all phases possess the same recoil-free fraction, the analysis of the experimental data was carried out by a least-squares computer minimization routine, using a sum of Lorentzian spectral components characterizing different iron phases.<sup>8</sup> The spectra were fitted using the NORMOS DO BRANT program.<sup>9</sup> The powder X-ray diffraction (XRD) data were obtained on a Rigaku model Geigerflex diffractometer using Cu K<sub>α</sub> radiation, scanning from 2 to 75° at a scan rate of 4° min<sup>-1</sup>. The values of the lattice parameters were obtained by a least-squares refinement using the method of Holland & Redfern.<sup>10,11</sup> The TPR (temperature programmed reduction) analysis was performed in a CHEM BET 3000 TPR using H<sub>2</sub> (8% in N<sub>2</sub>) with a heating rate of 10 °C min<sup>-1</sup>. The H<sub>2</sub> consumption was obtained after calibration of the TPR system using standard CuO. The TPD (temperature programmed desorption) was carried out using a HP quadrupole mass spectrometer to measure the O<sub>2</sub> desorbed during the heating (10 °C min<sup>-1</sup>) under vacuum (10<sup>-6</sup> torr). The hydrogen peroxide (Synth) decomposition was carried out with 11 mL of a H<sub>2</sub>O<sub>2</sub> solution (0.9 mol L<sup>-1</sup>) and 60 mg of the alloyed mixture, measuring the formation of gaseous O<sub>2</sub> in a volumetric glass system. For the oxidation of methylene blue (3.5 mL at 0.05 g L<sup>-1</sup>), 0.1 mL of H<sub>2</sub>O<sub>2</sub> 30% and 30 mg of the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures were added to the aqueous solutions (prepared with Millipore MilliQ water) under stirring. All reactions were carried out using magnetic stirring in a recirculating temperature controlled bath kept at 25 ± 1 °C. The oxidation of methylene blue was monitored via UV/Vis (Varian Cary 50 Conc). The hydrogen peroxide was added only after the adsorption equilibrium took place. The solution spectroscopic absorbance usually decreased only between 3 to 6%. After the reactions, the aqueous phases were analyzed for Fe and Mn by atomic absorption (Carl Zeiss Jena AAS).

## Results and Discussion

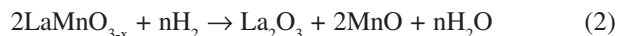
### *Characterization of the LaMnO<sub>3</sub> by TPR and TPD: oxygen availability for reaction*

In order to investigate the oxygen availability and reactivity for the transference to Fe<sup>0</sup>, the prepared LaMnO<sub>3</sub> was characterized by TPR (temperature programmed reduction) and O<sub>2</sub>-TPD (temperature programmed desorption). TPR analysis of LaMnO<sub>3</sub> (Figure 1a) showed two sets of peaks: (i) at 200-530 °C and (ii) at temperatures higher than 550 °C. The peaks at 200-530 °C have been

assigned to the reduction of  $\text{Mn}^{4+}$  and also to the reduction of some  $\text{Mn}^{3+}$  with loss of oxygen, according to the process:<sup>12</sup>

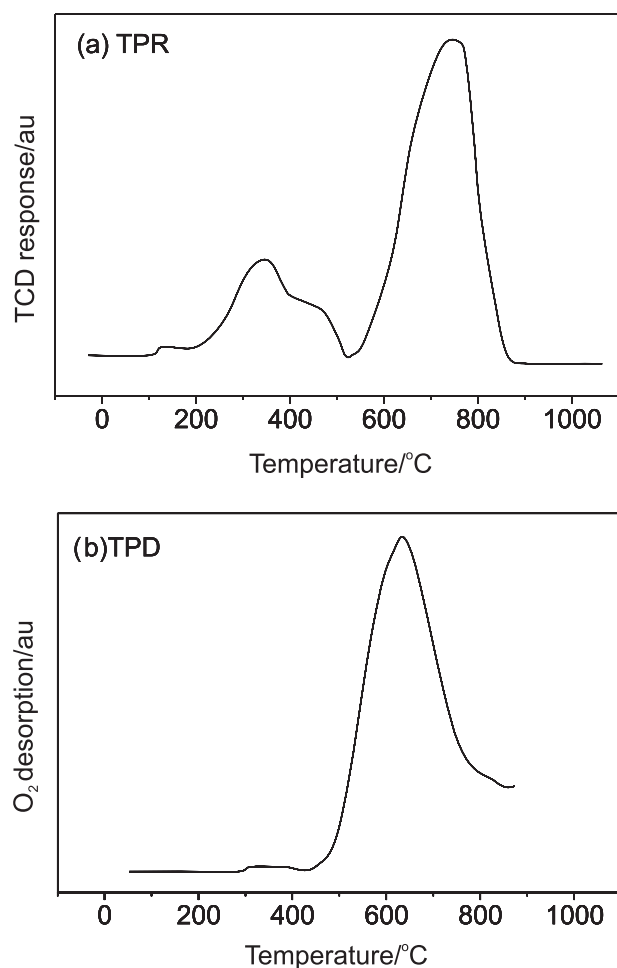


The high temperature TPR peak centered at 760 °C is related to the reduction of all  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$ , leading to the collapse of the perovskite structure to produce mainly  $\text{La}_2\text{O}_3$  and  $\text{MnO}$ :<sup>12</sup>



From the total hydrogen consumption, the oxygen stoichiometry obtained for the perovskite in this work was *ca.*  $\text{LaMnO}_{3.15}$ , which agrees with different values reported in the literature.<sup>13</sup>

The  $\text{O}_2$ -TPD experiment (Figure 1b) shows that oxygen is released from the perovskite structure at temperatures higher than 500 °C, as a broad  $\text{O}_2$  desorption peak centered at 650 °C can be observed. This  $\text{O}_2$ , named  $\beta$ -oxygen,<sup>14</sup> is



**Figure 1.** (a) Temperature programmed reduction, TPR, and (b) oxygen temperature programmed desorption, TPD, of  $\text{LaMnO}_3$ .

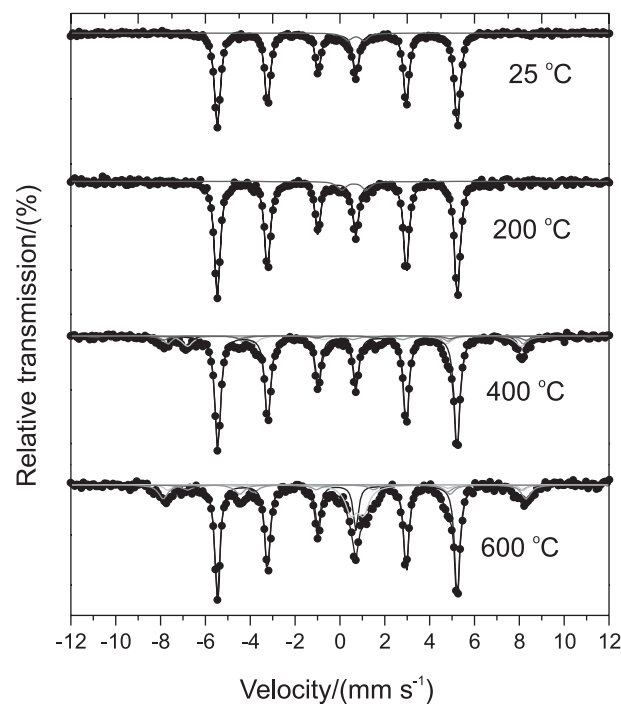
related to the desorption of non-stoichiometric oxygen and the reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$ . A shoulder near 800-900 °C is also observed, which has been assigned in the literature to the reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$ .<sup>14</sup>

Based on the TPR and TPD results, three temperatures were selected for the treatment of the mixtures  $\text{Fe}^0/\text{LaMnO}_3$ : 200 °C, where the perovskite begins to be reduced; 400 °C, where non-stoichiometric and some stoichiometric oxygen reacts without destroying the perovskite structure and 600 °C, where the perovskite structure can be strongly affected by  $\text{H}_2$ . Also, the thermal treatment of the  $\text{Fe}^0/\text{LaMnO}_3$  mixtures was carried out under argon flow to avoid non-interface reactions, for example the oxidation of  $\text{Fe}^0$  by  $\text{O}_2$  released by desorption, as seen in the TPD experiment.

#### Interface reactions in the system $\text{Fe}^0/\text{LaMnO}_3$

In order to produce a superficial interaction between the particles of  $\text{Fe}^0$  and the perovskite  $\text{LaMnO}_3$  but to avoid an extensive reaction, a very mild mechanical alloying by simple manual grinding for 60 s was used. Alloying for longer time or with higher energy can promote a significant reaction of iron metal with different oxides.<sup>15</sup>

Mössbauer spectra of the  $\text{Fe}^0/\text{LaMnO}_3$  mixtures after grinding (25 °C) and after thermal treatment at 200-600 °C are shown in Figure 2. The Mössbauer hyperfine parameters obtained from the spectra can be seen in Table 1.



**Figure 2.** Transmission room temperature Mössbauer spectra of the  $\text{Fe}^0/\text{LaMnO}_3$  mixtures treated at 25, 200, 400 and 600 °C under argon atmosphere.

**Table 1.** Mössbauer hyperfine parameters for the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures treated at 25, 200, 400 and 600 °C under argon atmosphere

Sample	Phases	Isomer shift ( $\delta$ ) / (mm s <sup>-1</sup> ) $\pm$ (0.05 mm s <sup>-1</sup> )	*Quadrupole splitting ( $\Delta$ ) / (mm s <sup>-1</sup> ) $\pm$ (0.05 mm s <sup>-1</sup> )	Hyperfine field ( $\Delta_{\text{HF}}$ ) / T $\pm$ (0.5 T)	Relative area / %	
Pure Fe <sup>0</sup>	Fe <sup>0</sup>	0.00	0.00	33.0	100	
Fe <sup>0</sup> /LaMnO <sub>3</sub> 25 °C	Fe <sup>0</sup>	0.00	0.00	33.0	97	
	Fe <sup>3+</sup> <sub>disperse</sub>	0.37	0.69	—	3	
Fe <sup>0</sup> /LaMnO <sub>3</sub> 200 °C	Fe <sup>0</sup>	0.00	0.00	33.0	96	
	Fe <sup>3+</sup> <sub>disperse</sub>	0.37	0.68	—	4	
Fe <sup>0</sup> /LaMnO <sub>3</sub> 400 °C	Fe <sup>0</sup>	0.00	0.00	33.0	75	
	Fe <sub>3</sub> O <sub>4</sub> [A]	0.35	0.02	49.1	18	
	[B]	0.66	0.18	46.0	—	
	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.32	-0.21	51.7	1	
	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	0.30	0.04	50.2	4	
	FeO	0.73	0.65	—	2	
	Fe <sup>0</sup> /LaMnO <sub>3</sub> 600 °C	Fe <sup>0</sup>	0.00	0.00	33.0	63
	Fe <sub>3</sub> O <sub>4</sub> [A]	0.35	0.02	49.1	11	
[B]	0.66	0.18	46.0	—		
	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.32	-0.21	51.7	2	
	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	0.30	0.04	50.2	11	
	FeO	0.73	0.65	—	13	

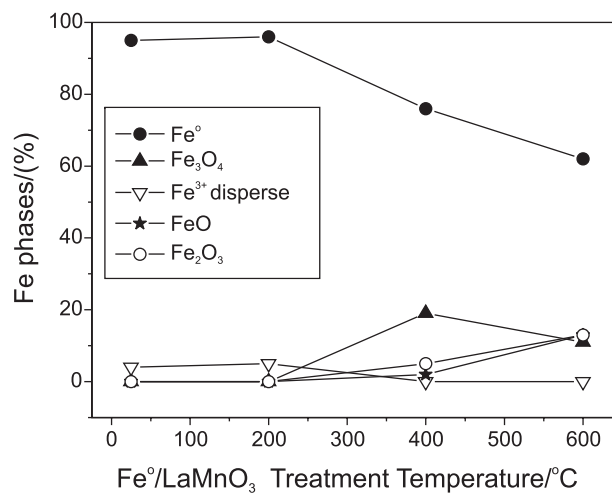
\*relative to  $\alpha$ -Fe

The commercial iron metal used in this work showed only a sextet with quadrupolar splitting of 33 T relative to Fe<sup>0</sup>. The Fe<sup>0</sup>/LaMnO<sub>3</sub> mixture after a simple manual grinding for 60s (25 °C) showed, besides the Fe<sup>0</sup> signal (97%), also a low intensity signal (3%) relative to Fe<sup>3+</sup><sub>disperse</sub>, with  $\delta$  0.37 and  $\Delta$  0.69 mm s<sup>-1</sup>. As pure Fe<sup>0</sup> ground by the same procedure did not show this signal for Fe<sup>3+</sup><sub>disperse</sub>, this result suggests that the simple grinding of Fe<sup>0</sup> with LaMnO<sub>3</sub> for 60 s led to some oxidation of the iron metal surface. Upon treatment at 200 °C no significant change was observed. On the other hand, at 400 and 600 °C the relative intensity of Fe<sup>0</sup> signal strongly decreased and new signals related to the Fe<sub>3</sub>O<sub>4</sub>, FeO,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phases appeared. Experiments with pure iron at 600 °C under argon flow did not show any significant reaction, ruling out any oxidation by impurities such as O<sub>2</sub> or H<sub>2</sub>O in the Ar gas.

The phase compositions for the different treatment temperatures can be better visualized in Figure 3. It can be observed that at 400 °C the Fe<sup>0</sup> is converted mainly to Fe<sub>3</sub>O<sub>4</sub> (18%). As the reaction was carried out under argon atmosphere, the oxygen to oxidize Fe<sup>0</sup> should come from the perovskite according to the process:<sup>5</sup>



At 600 °C, the relative Fe<sup>0</sup> signal intensity further decreases, indicating its consumption in the reaction. As the Fe<sub>3</sub>O<sub>4</sub> relative signal intensity decreases, the signals for FeO and Fe<sub>2</sub>O<sub>3</sub> (as  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) showed a significant increase. To explain the formation of these iron oxides, one can consider several processes taking place

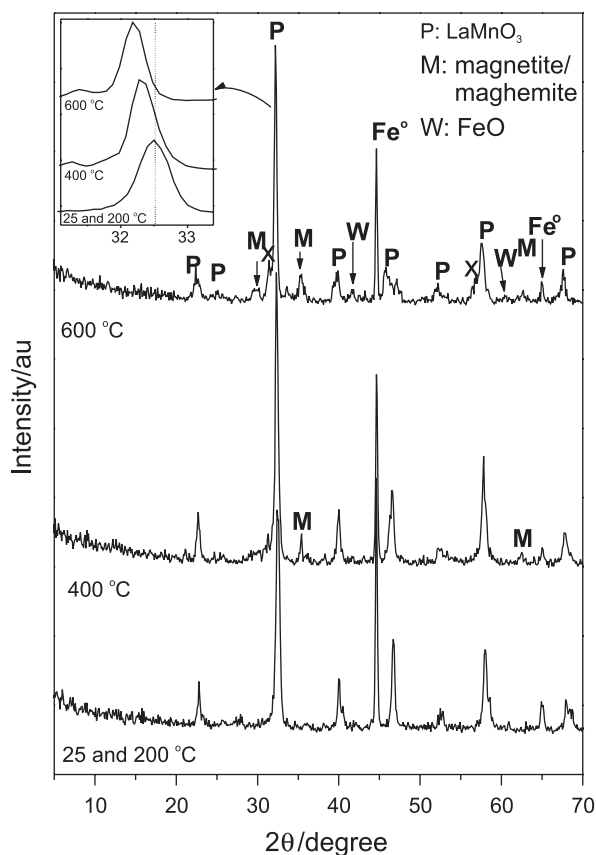
**Figure 3.** Mössbauer phase compositions of the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures thermally treated under argon at 200, 400 and 600 °C.

at 600 °C: (i) The oxidation of the Fe<sub>3</sub>O<sub>4</sub> by LaMnO<sub>3</sub> according to the process:



It should also be considered that Fe<sub>3</sub>O<sub>4</sub> can be oxidized by air even at room temperature to produce large quantities of maghemite.<sup>5</sup> Therefore, a significant part of the Fe<sub>2</sub>O<sub>3</sub> observed might have been formed after thermal treatment when the sample was exposed to air; (ii) The transformation of the maghemite  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> spinel cubic structure to the hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hexagonal structure, which is known to take place at temperatures near 520 °C.<sup>16</sup> (iii) The reaction of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> with Fe<sup>0</sup> to produce FeO, occurring at temperatures near 600 °C.<sup>17</sup>

Another process which could take place is the complete reduction of the LaMnO<sub>3</sub>, leading to the collapse of the perovskite structure. To investigate this possibility, the thermally treated Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures were also studied by powder X-ray diffraction (XRD). In Figure 4, typical peaks for the LaMnO<sub>3</sub> orthorhombic structure can be observed.<sup>18</sup>

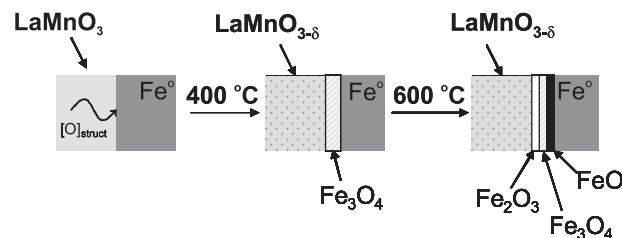


**Figure 4.** X-ray powder diffractograms of the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures after thermal treatment under argon at 200, 400 and 600 °C.

When the mixture Fe<sup>0</sup>/LaMnO<sub>3</sub> was thermally treated at 200 °C under argon, no significant change was detected. On the other hand, at 400 and 600 °C several changes were observed: (i) the relative intensity of the Fe<sup>0</sup> diffraction peaks progressively decreases. The ratio  $I_{\text{XRD}}(\text{LaMnO}_3)/I_{\text{XRD}}(\text{Fe}^0)$  ( $I_{\text{XRD}}(\text{Fe}^0)$  at  $2\theta$  ca. 45° and  $I_{\text{XRD}}(\text{LaMnO}_3)$  at  $2\theta$  ca. 32°) changes from 0.86 to 0.85, 1.54 and 1.67 for the mixtures treated at 25, 200, 400 and 600 °C, respectively. These results clearly indicate the consumption of the Fe<sup>0</sup> upon thermal treatment; (ii) The perovskite diffraction peaks shift to lower angles (Figure 4, detail), suggesting that the lattice parameters are changing after thermal treatment. The lattice parameters obtained for the sample at 25 and 200 °C are similar to the observed in the literature for the pure LaMnO<sub>3</sub> ( $a = 7.796$  Å,  $b = 5.540$  Å and  $c = 5.508$  Å),<sup>19</sup> indicating that at these conditions no significant change in

the perovskite structure takes place. On the other hand, after treatment at 400 and 600 °C, the XRD data suggest that the perovskite unit cell volume increased to 245.1 Å<sup>3</sup> ( $a = 7.689$  Å,  $b = 5.540$  Å and  $c = 5.753$  Å), likely due to the loss of oxygen from the structure; (iii) Estimation of the crystallite size using the Scherrer equation suggests that the perovskite crystals increase from 170 to 240 and 310 Å as the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixture is treated at 200, 400 and 600 °C respectively; (iv) Although the Mössbauer spectrum clearly shows the formation of Fe<sub>3</sub>O<sub>4</sub> at 400 °C, XRD only shows a small and broad peak related to Fe<sub>3</sub>O<sub>4</sub>, suggesting a highly dispersed phase. On the other hand, at 600 °C better crystallized Fe<sub>3</sub>O<sub>4</sub> and FeO were observed, with particle sizes of 103 and 135 Å estimated by the Scherrer equation; (v) No peaks for La<sub>2</sub>O<sub>3</sub> (at 27.2 and 31.6°, file 22-0369) or MnO (40.5, 34.9 and 58.7°, file 07-0230) could be detected, suggesting that the collapse of the perovskite structure does not take place significantly or it is producing highly dispersed/amorphous La<sub>2</sub>O<sub>3</sub> and MnO phases; (vi) It was also observed that the thermal treatment at 600 °C does not affect the surface area measured by the BET N<sub>2</sub> adsorption method, which was ca. 2 m<sup>2</sup> g<sup>-1</sup> for the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixture before and after thermal treatment.

Mössbauer and XRD data suggest that the perovskite LaMnO<sub>3.15</sub> can transfer oxygen to Fe<sup>0</sup> by an interface reaction producing new iron oxide phases. Based on these results, a very simple and idealized scheme to explain the surface reaction between LaMnO<sub>3+δ</sub> and Fe<sup>0</sup> can be proposed:



**Figure 5.** Scheme for the oxygen transfer from LaMnO<sub>3</sub> to Fe<sup>0</sup>, forming different iron oxide phases.

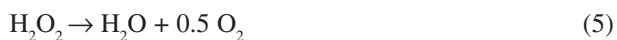
After thermal treatment, the particles shown in Figure 5 can be separated by breaking the interface and exposing both surfaces, the reduced LaMnO<sub>3</sub> and the oxidized Fe<sup>0</sup>, which have an important effect on the catalytic properties of the materials.

#### Effect of thermal treatment on the properties of Fe<sup>0</sup>/LaMnO<sub>3</sub> towards H<sub>2</sub>O<sub>2</sub> reactions

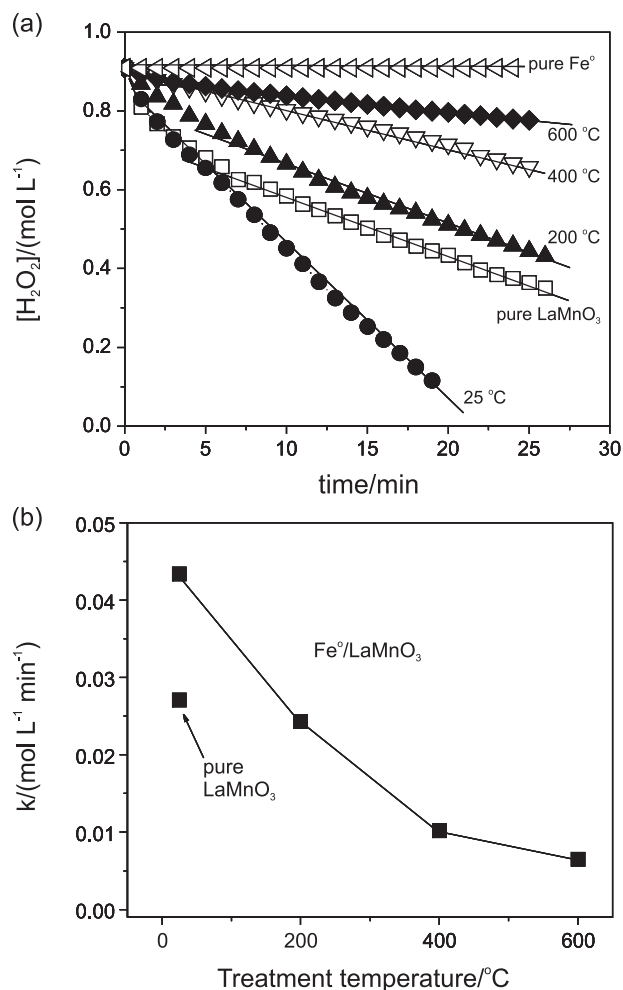
The Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures treated at different temperatures were studied to promote two reactions: (i) the decomposition of H<sub>2</sub>O<sub>2</sub> to O<sub>2</sub> and (ii) the oxidation of methylene blue with H<sub>2</sub>O<sub>2</sub>.



The hydrogen peroxide decomposition (equation 5) is a versatile probe reaction to investigate the activity of perovskite catalysts, as (i) the experimental set-up is simple, (ii) it has been well investigated for different perovskites,<sup>19-22</sup> (iii) Mn-containing perovskites are especially active for this reaction,<sup>23-25</sup> and (iv) the activity is very sensitive to changes in the transition metal oxidation state and oxygen vacancies on the surface.



The results obtained for the peroxide decomposition in the presence of the different Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures can be seen in Figure 6. The linear behavior of the decomposition plots (Figure 6a) suggests a pseudo zero order dependence on the H<sub>2</sub>O<sub>2</sub> concentration under the reaction conditions employed ( $V_{\text{decomp}} = -k_{\text{decomp}} [\text{H}_2\text{O}_2]^0$ ). The pseudo-zero order reaction rate constants calculated from the slope of the decomposition plots are shown in Figure 6b.



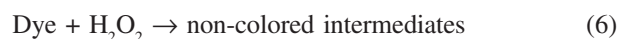
**Figure 6.** (a) Hydrogen peroxide decomposition for the pure LaMnO<sub>3</sub>, pure Fe<sup>0</sup> and Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures treated at 25-600 °C and (b) pseudo-zero order reaction rates ( $[\text{H}_2\text{O}_2]=0.9 \text{ mol L}^{-1}$ , 11 mL, 60 mg catalyst).

It can be observed that the pure LaMnO<sub>3</sub> perovskite is highly active for H<sub>2</sub>O<sub>2</sub> decomposition. This high activity has been reported in the literature for different Mn perovskites and was assigned to the presence of high oxidation state species, *e.g.* Mn<sup>4+</sup>.<sup>23,25</sup> It has also been reported that oxygen vacancies on the perovskite surface<sup>21</sup> can play an important role for the H<sub>2</sub>O<sub>2</sub> decomposition. Figure 6 shows that, although Fe<sup>0</sup> is completely inactive for the peroxide decomposition, its simple mixture with LaMnO<sub>3</sub> caused a significant increase on the activity. Mössbauer spectroscopy and XRD analyses of the mixture did not show any bulky significant change in Fe<sup>0</sup> and LaMnO<sub>3</sub>. Therefore, this increase in reactivity suggests that a surface reaction should have taken place by the simple contact of the Fe<sup>0</sup> and the perovskite phases, likely by a superficial oxygen transfer from the perovskite to Fe<sup>0</sup>. This oxygen transfer should generate two different species: (i) oxygen vacancies on the perovskite surface and (ii) Fe oxidized species on the Fe<sup>0</sup> surface. Both species can catalyze H<sub>2</sub>O<sub>2</sub> decomposition. Previous work has also shown that a simple mixture of Fe<sup>0</sup> with Fe<sub>3</sub>O<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub> produced an increase on the activity for H<sub>2</sub>O<sub>2</sub> decomposition.<sup>4,5</sup> Therefore, the iron oxides formed might have an important contribution to increase the reaction rate.

On the other hand, after thermal treatment at 200, 400 and 600 °C, a progressive decrease in the decomposition activity is observed. Although the reasons for this decrease are not clear, one can envisage that at higher temperatures the oxygen transfer from the perovskite should significantly reduce the concentration of Mn<sup>4+</sup><sub>surf</sub> and also Mn<sup>3+</sup><sub>surf</sub> species on the perovskite to produce Mn<sup>2+</sup>, leading to a decrease on the H<sub>2</sub>O<sub>2</sub> decomposition activity.

The effect of the thermal treatment on the activity of the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures for the oxidation of organic compounds in aqueous medium with H<sub>2</sub>O<sub>2</sub> was also investigated. In this study, methylene blue (MB) was used as a probe molecule, as it shows several interesting features: (i) it is highly soluble in water, (ii) its oxidation can be simply monitored by spectrophotometric measurements and (iii) it simulates the behavior of textile dyes, which are an important class of industrial contaminant.

The oxidation of methylene blue was monitored by the discoloration rate, which is related to the first oxidation steps to produce non-colored intermediates



These discoloration measurements give important information on the rate of formation of reactive oxidation

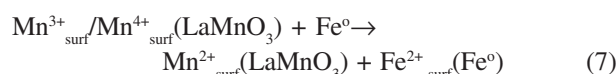
species. Some processes that could interfere on the reaction monitoring by discoloration, such as adsorption and reduction of the dye by Fe<sup>0</sup>, are minimized by the use of MB, as (i) it is a cationic molecule which decreases its adsorption on the LaMnO<sub>3</sub> perovskite and on the iron oxides due to their high PZC (point zero charge)<sup>26</sup> and (ii) MB is not easily reduced by pure iron metal.<sup>27</sup>

The discoloration plots obtained for pure LaMnO<sub>3</sub>, pure Fe<sup>0</sup> and the Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures treated at 25, 200, 400 and 600 °C are shown in Figure 7. A kinetic treatment using a  $\ln A_t/A_0$  (where  $A_t$  = absorbance at the time t and  $A_0$  = absorbance at time zero) versus time produced fairly straight lines, suggesting that the kinetics of the discoloration process under the reaction conditions employed can be approximated to a first order dependence on the dye concentration  $V_{\text{discol}} = k_{\text{discol}} [\text{dye}]^{-1}$ .

It can be observed that pure LaMnO<sub>3</sub> shows some activity, producing a discoloration of ca. 10% after 120 min. Pure Fe<sup>0</sup> also showed a similar discoloration activity. However, this discoloration is mainly due to the reduction of methylene blue by Fe<sup>0</sup>, as suggested by blank experiments without H<sub>2</sub>O<sub>2</sub>. It is interesting to observe that the simple mixture of LaMnO<sub>3</sub>

with Fe<sup>0</sup> produced a remarkable increase on the activity for the discoloration. Upon thermal treatment at 200 °C, no significant difference was observed. On the other hand, after treatment at 400 and 600 °C, a further increase on the discoloration activity was observed. Atomic absorption analyses for Fe and Mn ions in all solutions after reaction did not show any significant metal content, suggesting the presence of a heterogeneously catalyzed process.

A simple proposal to understand these results is to consider the reaction between the perovskite and Fe<sup>0</sup> to produce Mn<sup>2+</sup><sub>surf</sub> and Fe<sup>2+</sup><sub>surf</sub> species, according to the process:



It is well known that Fe<sup>2+</sup><sub>surf</sub> species are active for the Fenton reaction.<sup>4</sup> Previous work in our group<sup>4,5</sup> suggested that the effect of grinding Fe<sub>3</sub>O<sub>4</sub> with Fe<sup>0</sup> is the reduction of Fe<sub>3</sub>O<sub>4</sub> to form higher concentrations of Fe<sup>2+</sup><sub>surf</sub> species active for the Fenton chemistry. Also, several works in the literature showed that Mn<sup>2+</sup> species, soluble or in solid matrix, are active to promote the Fenton reaction.<sup>28-30</sup> Therefore, the oxygen transfer from LaMnO<sub>3</sub> to Fe<sup>0</sup> has two important effects for the H<sub>2</sub>O<sub>2</sub> reactions, *i.e.* it decreases the activity for the undesired peroxide decomposition and it produces M<sup>2+</sup> species active for the Fenton chemistry.

## Conclusions

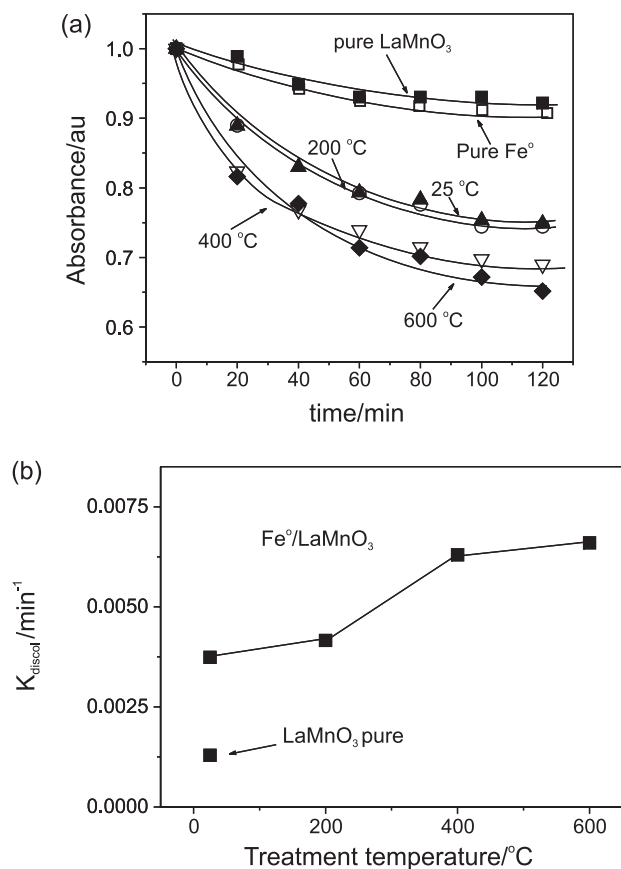
The perovskite LaMnO<sub>3,15</sub> can transfer oxygen to Fe<sup>0</sup> by an interface reaction producing a partially reduced perovskite LaMnO<sub>3,δ</sub> and highly dispersed iron oxides, mainly Fe<sub>3</sub>O<sub>4</sub>, on the Fe<sup>0</sup> surface. As the mixtures Fe<sup>0</sup>/LaMnO<sub>3</sub> are treated at 200, 400 and 600 °C, the reactivity towards H<sub>2</sub>O<sub>2</sub> decomposition decreases, whereas the activity for the oxidation of methylene blue increases. These results can be discussed in terms of a decrease on the concentration of Mn<sup>4+</sup><sub>surf</sub> and Mn<sup>3+</sup><sub>surf</sub> (active for H<sub>2</sub>O<sub>2</sub> decomposition) with an increase on the Mn<sup>2+</sup><sub>surf</sub> and Fe<sup>2+</sup><sub>surf</sub> species, active for the Fenton reaction.

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**Figure 7.** (a) Discoloration activity and (b) first order reaction rates for the oxidation of methylene blue with pure LaMnO<sub>3</sub>, pure Fe<sup>0</sup> and Fe<sup>0</sup>/LaMnO<sub>3</sub> mixtures treated at 25-600 °C (dye 3.5 mL at 0.05 g L<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> 0.28 mol L<sup>-1</sup>, 30 mg catalyst).

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