LaFeₓMnᵧMo₂O₉ Catalysts for the Oxidation of Volatile Aromatic Organic Contaminants

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Novas perovskitas mistas LaFeₓMnᵧMo₂O₉ foram preparadas, caracterizadas e investigadas como catalisadores para a oxidação total de tolueno, usado como composto orgânico aromático volátil (COV aromático) modelo. As perovskitas foram caracterizadas por DRX (Difratometria de Raios X), RTP (Redução a Temperatura Programada), determinação de área superficial BET e espectroscopia Mössbauer. Os dados obtidos indicaram a formação da fase perovskita e a incorporação de todos os metais na estrutura. As reações catalíticas foram realizadas em um sistema de Reação a Temperatura Programada com tolueno (1000 ppm) e ar sintético em fase gasosa. Foi observado que a oxidação do tolueno inicia-se a 280 °C e que Mn é o principal responsável pela atividade catalítica. No entanto, a presença de pequenas quantidades de Fe (LaFe₀.₂₇Mn₀.₇₃O₃) resulta em um importante aumento nessa atividade. Estudos de tempo de vida mostraram que os catalisadores são estáveis mesmo após 100 h de reação a 400 °C e nenhuma alteração estrutural significativa foi observada por DRX e Mössbauer.

New mixed perovskites LaFeₓMnᵧMo₂O₉ were prepared, characterized, and investigated as catalysts for the total oxidation of the model aromatic VOC (Volatile Organic Compound), toluene. The perovskites were characterized by XRD (X-Ray Diffractometry), Mössbauer spectroscopy, TPR (Temperature Programmed Reduction) and BET surface area determination. The results suggested the formation of the perovskite phase with incorporation of all metals in the structure. The catalytic studies were carried out in a Temperature Programmed Reaction system with toluene (1000 ppm) and synthetic air in the gas phase. It was observed that the oxidation of toluene starts at temperature as low as 280 °C and that Mn is responsible for most of the catalytic activity. However, the presence of small amounts of Fe (LaFe₀.₂₇Mn₀.₇₃O₃) leads to an increase in this activity. Stability studies showed that these perovskite catalysts are stable even after 100 h reaction at 400 °C with no significant structural change, as observed by XRD and Mössbauer analyses.

Keywords: lanthanum iron perovskite, toluene oxidation, catalytic oxidation, manganese, molybdenum

Introduction

Perovskite type oxides, ABO₃, have been extensively investigated as catalysts for several processes including fuel cells, water dissociation, hydrogenation and hydrogenolysis, ammonia oxidation and NO reduction. Several reviews covering these fields can be found in the literature. Perovskites, especially LaMnO₃, have also been used in environmental applications, e.g. the oxidation of hydrocarbons, chlorinated organics and H₂O₂ reactions. LaMnO₃ shows good stability and flexible oxygen stoichiometry (δ) with different Mn oxidation states, i.e. Mn⁷⁺, Mn⁵⁺, Mn⁴⁺, which strongly affects the catalytic behavior. Also, the isomorphic substitution of metals in the perovskite structure allows a control of the catalytic properties of the material. Several LaMnO₃
derivatives, i.e. \( \text{La}_{1-x} \text{A}_x \text{Mn}_{1-y} \text{M}_y \text{O}_3 \) (where A can be a lanthanide, actinide, alkaline or earth alkaline metal and M can be a transition metal such as Co, Ni, etc.) have already been investigated.\(^{13,14}\)

In this work we studied for the first time the isomorphic substitution of Mn in the \( \text{LaMnO}_3 \) structure by different amounts of Fe and Mo to produce the series of perovskites \( \text{LaFe}_x \text{Mn}_y \text{Mo}_z \text{O}_3 \). The Fe and Mo can also vary their oxidation states and this property can improve the catalytic activity in oxidation processes. These perovskites were characterized in detail and used as catalysts for the total oxidation of toluene, a model of volatile aromatic contaminants.

**Experimental**

All chemicals were obtained from Sigma-Aldrich and used with no further purification. The perovskites were prepared by the reaction of 0.5 mol of citric acid (CA) dissolved in 2 mol of water at 60 °C with 1 mmol of \( \text{La(NO}_3\text{)}_3.6\text{H}_2\text{O} \) and different proportions of the other metals, such as \( x \text{mmol of Fe(NO}_3\text{)}_3.9\text{H}_2\text{O}, y \text{mmol of Mn(NO}_3\text{)}_2.4\text{H}_2\text{O} \) and \( z \text{mmol of Mo(acac)}_2\text{O}_2 \), in order to produce the desired stoichiometry, \( \text{LaFe}_x \text{Mn}_y \text{Mo}_z \text{O}_3 \). The mixture was stirred for about 2 h, until a clear orange solution of the stable metal–CA complexes was obtained. After complete dissolution, 400 mmol of ethyleneglycol (EG) were added and the solution was continuously stirred while the temperature was slowly increased to 90 °C. This step removed the excess of water and allowed the polyesterification reaction between CA and EG to be further activated. The prolonged heating at 90 °C occurred over 7 h and resulted in a viscous orange mass.\(^{12}\) This resin was then treated at 400-450 °C in air over 2 h for carbonization. The final product, a dark brown powder, was ground and then treated at 400-450 °C in air over 2 h for carbonization. This step resulted in a viscous orange mass.\(^{12}\) This resin was then treated at 400-450 °C in air over 2 h for carbonization. The final product, a dark brown powder, was ground and then calcined at 800 °C in air for 6 h. The catalysts were characterized by powder XRD, TPR (temperature programmed reduction), Mössbauer spectroscopy, BET surface area determination and thermal analysis. The surface area was determined using 22 cycles of N\(_2\) adsorption/desorption in an Autosorb 1 Quantachrome instrument. The \(^{57}\)Fe Mössbauer spectroscopy experiments were carried out in the transmission geometry on a constant-acceleration conventional spectrometer with a \(^{57}\)Co/Rh source at room temperature (RT), using α-Fe as a reference. The powder XRD data were obtained in a Philips X′Pert equipment using Cu K\(_α\) or Co K\(_α\) radiation scanning from 2 to 80° at a scan rate of 4° min\(^{-1}\). The TPR analysis was performed in a CHEM BET 3000 TPR using \( \text{H}_2 \) (8% in \( \text{N}_2 \)) with a heating rate of 10 °C min\(^{-1}\). The \( \text{H}_2 \) consumption was determined after calibration of the TPR system using a CuO standard. The thermal analysis was carried out on a Shimadzu DTG-60 equipment, with a constant heating rate of 10 °C min\(^{-1}\) under air flow (50 mL min\(^{-1}\)).

The catalytic tests were carried out with toluene in the gas phase (ca. 1% in air at 30 mL min\(^{-1}\)), introduced in the reaction stream by a saturator with a temperature of 0 °C. The catalyst (10 mg) was placed in a quartz tube (0.5 mm i.d.) in the central part of a furnace and heated to the reaction temperatures at 5 °C min\(^{-1}\). Based on the catalyst bed volume, a gas hourly space velocity (GHSV) of approximately 40000 h\(^{-1}\) was estimated. The reaction products were analyzed on-line by FID-equipped gas chromatography (Shimadzu 17A).

**Results and Discussion**

The perovskites were prepared in two series with different stoichiometries of Fe, Mn and Mo: (i) the Fe-Mn (\( \text{LaFe}_x \text{Mn}_y \text{O}_3 \)) and (ii) the Fe-Mn-Mo perovskites (\( \text{LaFe}_x \text{Mn}_y \text{Mo}_z \text{O}_3 \)). The results of XRD analyses for the \( \text{LaFe}_x \text{Mn}_y \text{O}_3 \) and \( \text{LaFe}_x \text{Mn}_y \text{Mo}_z \text{O}_3 \) perovskites are shown in Figure 1.

The main peaks in Figure 1(a) are related to the perovskite phase, e.g. \( \text{LaMnO}_3 \), 20 22.9 (d=3.88, (110)), 32.6 (d=2.74, (211)), 40.2 (d=2.24, (200)), 46.9 (d=1.94, (220)), 52.7 (d=1.63, (211)), 58.1 (d=1.59, (211)) and 68.2° (d=1.37, (422)).\(^{15}\) It can be observed, however, a gradual shift of the XRD peaks to lower diffraction angles as a function of the increasing concentration of iron. Such change is also present in the cell parameters determined for perovskites having different compositions (see Table 1), suggesting a gradual incorporation of Fe into the perovskite structures. The crystal structures were best adjusted to a pseudo-cubic arrangement.\(^{16,17}\) XRD results for the \( \text{LaFe}_x \text{Mn}_y \text{Mo}_z \text{O}_3 \) perovskite (Figure 1(b) and Table 1) are very similar, which also indicates the incorporation of the Mo into the structure. Both crystallite size and BET surface area do not change significantly for the \( \text{LaFe}_x \text{Mn}_y \text{O}_3 \) and \( \text{LaFe}_x \text{Mn}_y \text{Mo}_z \text{O}_3 \) series varying between 120-144 nm and 11-15 m\(^2\) g\(^{-1}\) (Table 1).

Mössbauer spectra of the \( \text{LaFe}_x \text{Mn}_y \text{O}_3 \) and \( \text{LaFe}_{0.90} \text{Mn}_{0.10} \text{Mo}_3 \text{O}_3 \) perovskites are shown in Figure 2.

The spectra of the \( \text{LaFe}_{0.27} \text{Mn}_{0.73} \text{O}_3 \) and \( \text{LaFe}_{0.54} \text{Mn}_{0.46} \text{O}_3 \) perovskites showed only doublets with isomer shifts (\( \Delta \)) equal to 0.33 mm s\(^{-1}\), and quadrupole splittings (\( \Delta \)) of 52 mm s\(^{-1}\) and 62 mm s\(^{-1}\) respectively, likely related to octahedral Fe\(^{3+}\) dispersed in the perovskite structure. As seen in Figure 2, this pattern splits into sextets for the higher concentration of Fe. The \( \text{LaFe}_{0.90} \text{Mn}_{0.10} \text{O}_3 \) perovskite, for example, shows a signal with hyperfine
parameters at $\delta$ 0.37 mm s$^{-1}$, $\Delta$ -0.05 mm s$^{-1}$ and magnetic hyperfine field ($H_{hf}$) 51.3 T with a relative area of 47%, assigned to well crystallized LaFeO$_3$. A second sextet at $\delta$ 0.37 mm s$^{-1}$, $\Delta$ 0.05 mm s$^{-1}$ and $H_{hf}$ 49.2 T is also observed with a relative area of 53%. This is identified as poorly crystallized LaFeO$_3$ probably due to small particle size or to the presence of Mn.

The results for the Mo-containing LaFe$_{0.90}$Mn$_{0.08}$Mo$_{0.02}$O$_3$ perovskite are very similar (Figure 2), but the relative intensity of the more crystalline phase is lowered down to 36% (0.36 mm s$^{-1}$, $\Delta$ -0.05 mm s$^{-1}$ and $H_{hf}$ 50.9 T) with a slight increase to 64% of the poorly crystallized phase ($\delta$ 0.37 mm s$^{-1}$, $\Delta$ 0.09 mm s$^{-1}$ and $H_{hf}$ 48.4 T). These results suggest that the introduction of Mo into the perovskite structure induces a loss of crystallinity. The presence of a higher Mo concentration apparently induces a more significant disorder in the perovskite structure, producing a segregation of Fe$^{3+}$.

Table 1. Surface area, crystallite size and cell parameters for the synthesized perovskites

<table>
<thead>
<tr>
<th>Perovskite</th>
<th>Surface area / (m$^2$ g$^{-1}$)</th>
<th>Crystallite size* / Å</th>
<th>Cell Parameters* / Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a=b=c / Å</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>15</td>
<td>144</td>
<td>3.885(2)</td>
</tr>
<tr>
<td>LaFe$<em>{0.27}$Mn$</em>{0.73}$O$_3$</td>
<td>13</td>
<td>143</td>
<td>3.913(2)</td>
</tr>
<tr>
<td>LaFe$<em>{0.54}$Mn$</em>{0.46}$O$_3$</td>
<td>14</td>
<td>141</td>
<td>3.913(2)</td>
</tr>
<tr>
<td>LaFe$<em>{0.90}$Mn$</em>{0.10}$O$_3$</td>
<td>11</td>
<td>142</td>
<td>3.944(1)</td>
</tr>
<tr>
<td>LaFe$<em>{0.90}$Mn$</em>{0.08}$Mo$_{0.02}$O$_3$</td>
<td>16</td>
<td>124</td>
<td>3.935(7)</td>
</tr>
<tr>
<td>LaFe$<em>{0.90}$Mn$</em>{0.05}$Mo$_{0.05}$O$_3$</td>
<td>15</td>
<td>120</td>
<td>3.949(1)</td>
</tr>
<tr>
<td>LaFe$<em>{0.90}$Mn$</em>{0.01}$Mo$_{0.09}$O$_3$</td>
<td>15</td>
<td>123</td>
<td>3.946(1)</td>
</tr>
</tbody>
</table>

*Obtained by the Scherrer equation; **obtained by the Fullprof program.

Figure 1. X-ray diffraction patterns (Cu K$\alpha$) of the different (a) LaFe$_x$Mn$_y$O$_3$ perovskites, and (b) LaFe$_x$Mn$_y$Mo$_z$O$_3$ perovskites.

Figure 2. $^{57}$Fe Room-temperature Mössbauer spectra of LaFe$_{0.90}$Mn$_{0.08}$O$_3$ and LaFe$_{0.90}$Mn$_{0.08}$Mo$_{0.02}$O$_3$ perovskites.
species. This is detected as an additional signal at $\delta 0.23$ mm s$^{-1}$ and $\Delta 0.62$ mm s$^{-1}$ with a small relative spectral area of 7%.

Temperature Programmed Reduction (TPR) experiments were performed to investigate the reducibility of the different perovskites. The TPR profile for LaMnO$_3$ (Figure 3) showed two sets of peaks: Peak 1 at 300-530 °C, assigned to the reduction of Mn$^{4+}$ and some Mn$^{3+}$, and Peak 2 at temperatures higher than 600 °C, due to the reduction of Mn$^{3+}$ to produce MnO, according to equation 1:

$$2\text{LaMnO}_3 + n\text{H}_2 \rightarrow \text{La}_2\text{O}_3 + 2\text{MnO} + n\text{H}_2\text{O} \quad (1)$$

Such TPR profile is similar to previously published results for LaMnO$_3$. TPR results for the LaFe$_{0.54}$Mn$_{0.46}$O$_3$ sample (Figure 3) exhibit the same Peak 1 reduction features, but two important characteristics have changed: (i) Peak 2 has shifted to lower temperature (~700 °C), with a significant decrease in peak area, and (ii) a new reduction feature appears, starting at temperatures near 800 °C. The latter is likely related to the reduction of the Fe species. Thus, the reduction of iron and the formation of Fe$^0$ seem to occur only at temperatures above 800 °C, which is when the perovskite structure collapses. Such a remarkable thermal stability of iron in the perovskite structure has already been documented in the literature. The smaller peaks for the TPR profiles of D, E and F samples (Figure 3) in the temperature range 300-600 °C are likely related to the reduction of the molybdenum and manganese species present only in small amounts.

**Catalytic oxidation of toluene**

The perovskites were investigated as catalysts for the total oxidation of aromatic VOCs, using toluene as a probe molecule (equation 2).

$$\text{C}_6\text{H}_5\text{CH}_3 + 9\text{O}_2 \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O} \quad (2)$$

To compare the activity of the different perovskites, TPRe (Temperature Programmed Reaction) experiments were performed. In the TPRe experiments, a mixture of toluene/air is passed through the catalyst and the reaction temperature is increased from 25 to 450 °C at 5 °C min$^{-1}$. The TPRe results for the different perovskites are shown in Figure 4.

All perovskites were active to oxidize toluene. GC analyses did not show any new peak during TPRe, suggesting that, under the analysis conditions, the only products formed were CO$_2$ and H$_2$O. According to Figure 4, the perovskite LaMnO$_3$ showed an oxidation on-set temperature (temperature where the oxidation starts) of ca. 318 °C.

The importance of manganese in the perovskite structure is likely related to the possibility to vary the Mn oxidation state within the Mn$^{2+} \rightarrow$ Mn$^{4+}$ range, allowing a very flexible oxygen stoichiometry ($\delta$). According to the Mars van Krevlin mechanism, this flexible stoichiometry should be very important for the catalytic activity, as the oxidation occurs in two steps: the reaction and the regeneration.

$$\begin{align*}
\text{LaMnO}_3 + \text{Organic} & \rightarrow x\text{CO}_2 + y\text{H}_2\text{O} + \text{LaMnO}_3 - \delta \\
\text{LaMnO}_3 - \delta + \text{O}_2 & \rightarrow \text{LaMnO}_3 
\end{align*}$$

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**Figure 3.** Temperature programmed reduction (TPR) profile of A) LaMnO$_3$, B) LaFe$_{0.54}$Mn$_{0.46}$O$_3$, C) LaFe$_{0.90}$Mn$_{0.10}$O$_3$, D) LaFe$_{0.90}$Mn$_{0.08}$Mo$_{0.02}$O$_3$, E) LaFe$_{0.90}$Mn$_{0.05}$Mo$_{0.05}$O$_3$, F) LaFe$_{0.90}$Mn$_{0.01}$Mo$_{0.09}$O$_3$.

**Figure 4.** TPRe oxidation of toluene in the presence of the different perovskite catalysts.
It is interesting to observe that the presence of small amounts of Fe (Fe\(_{0.27}\)) caused a significant decrease in the on-set temperature, indicating an increase in the catalytic activity (Figure 4). On the other hand, if the Fe concentration increases (Fe\(_{0.54}\) and Fe\(_{0.90}\)), the on-set temperature strongly increases, suggesting a decrease in the catalytic activity. This effect of substitution of Fe on the catalytic activity of the perovskites can be observed in Figure 5(a).

The reasons for this effect are not clear. The obtained results suggest that Mn is the main species involved in the catalytic cycle. The improvement of the catalytic activity in the presence Fe at low concentrations (i.e. Fe\(_{0.27}\)) could be related to the creation of surface and structural defects which can increase the perovskite reactivity towards toluene and oxygen. At high Fe concentration (e.g. Fe\(_{0.90}\)), the loss of the active Mn and the increase of the perovskite thermal stability can lead to a decrease on the catalytic activity. However, a more detailed investigation is necessary for a better understanding of the reaction mechanism.

Figure 5(b) shows the effect of Mo on the catalytic activity of the perovskites. It can be observed that the substitution of Mn by Mo caused a significant increase in the onset oxidation temperature, which means a decrease in the catalytic activity of the perovskite. This result again suggests that, in the perovskite LaFe\(_{0.90}\)Mn\(_{0.10}\)O\(_3\), an important part of the catalytic activity is related to the presence of Mn. Figure 5(b) also suggests that the activity of the element Mo in the perovskite structure is much smaller compared to Mn.

Stability studies were performed for the LaMnO\(_3\) and LaFe\(_{0.27}\)Mn\(_{0.73}\)O\(_3\) perovskites with a mixture of toluene/air passing through the catalyst at 400 °C for 100 hours. It was possible to observe that the perovskites were completely stable under these conditions. The catalysts

![Figure 5. On-set temperature for the oxidation of toluene: (a) Effect of the Fe content on the LaFe\(_x\)Mn\(_{1-x}\)O\(_3\) perovskite catalysts, and (b) effect of the Mo content on the LaFe\(_{0.90}\)Mn\(_{0.10}\)O\(_3\) perovskite catalysts.](image)

![Figure 6. X-ray diffraction patterns (Co K\(_\alpha\)) of (a) the LaMnO\(_3\) perovskite before and after the life time test, and (b) the LaFe\(_{0.27}\)Mn\(_{0.73}\)O\(_3\) perovskite before and after the life time test.](image)
obtained after these life time tests were characterized by XRD, and the results for the LaMnO₃ and LaFe₀.27Mn₀.73O₃ perovskites are shown in Figure 6.

After 100h reaction at 400 °C, the catalyst kept the XRD pattern of the perovskite phase (Figure 6). However, in the expanded details, small shifts of the XRD peaks to higher diffraction angles were observed after the reactions. These shifts could indicate that, during the reaction, the perovskite looses oxygen to produce the non-stoichiometric phases LaMnO₃₋ₓ. These non-stoichiometries are commonly observed in perovskite structures.¹⁰,²⁰,²¹ The shift seems more pronounced for LaMnO₃ (Figure 6(a)) compared to LaFe₀.27Mn₀.73O₃ (Figure 6(b)), which could be related to the higher stability produced in the perovskite by the presence of Fe. Broad and low intensity peaks between 20-30° can also be observed in Figure 6. Although the origin of these peaks is not clear, they could be related to the formation of carbon deposits during the reaction. In fact, TG analyses of the catalyst LaFe₀.27Mn₀.73O₃ after reaction (not shown) showed small weight losses (ca. 0.2%) between 270 and 350 °C, which could be related to the oxidation of surface deposits of amorphous carbon.

The catalyst LaFe₀.27Mn₀.73O₃ was analyzed by Mössbauer spectroscopy before and after the reaction at 400 °C for 100 h (Figure 7(a)). The spectra showed only a central doublet, with very similar hyperfine parameters before and after reaction. Additionally, no significant modification was observed in the Mössbauer spectrum of the catalyst LaFe₀.60Mn₀.40O₃ tested at higher temperatures, i.e. 600 °C, in the TPRe experiments. These results suggest that, under the reaction conditions employed in this work, no significant change around the Fe site in the perovskite structure takes place.

Conclusions

Perovskites LaFeₓMnᵧMo₃O₉ (x=0.27-0.90, y=0.10-0.73 and z=0.02-0.09) were all active for the catalytic total oxidation of toluene. Stability studies showed no deactivation of the catalyst even after 100 h of reaction at 400 °C.

As Mn in LaMnO₃ is replaced by Fe (e.g. Fe₀.54 and Fe₀.90), the catalytic activity decreases. This result is likely related to the higher activity of LaMnO₃ compared to LaFeO₃ for total oxidation, as reported in the literature.²²,²³ On the other hand, the higher activity observed for the perovskite LaFe₀.27Mn₀.73O₃ suggests a special effect of the combination of small amounts of Fe with Mn. However, more detailed studies are necessary to understand the effect of Fe in the catalytic reaction.

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