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LaBO$_3$ (B: Mn, Fe, Co, Ni, Cu and Zn) Catalysts for CO + NO Reaction

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Abstract

A series of transition metals LaBO$_3$ perovskites (B= Mn, Fe, Co, Ni, Cu and Zn) has been synthesized and tested as catalysts for simultaneous removal of CO and NO in a fixed bed reactor. To improve the catalytic activity of LaFeO$_3$, as the most active formulation, it has been modified by using other active metals (Mn, Co and Cu) for partial substitution of Fe in the perovskite formulation (LaFe$_{0.7}$M$_{0.3}$O$_3$). The results revealed that Mn substitution improves significantly the catalytic activity because increases the Mn (IV) to Mn (III) ratio leading to the generation of a large amount of structural defects and, also, because increases the amount of reducible active sites.

Keywords. Perovskite, NOx reduction, NO+CO reaction, Catalytic reduction, Air pollution.

Introduction

The removal of CO and NO has attracted a great attention because of their presence in mobile and static exhaust sources. Photochemical smog and acid rain formation are the main problems caused by NOx emissions. For the removal of NOx, different strategies including selective catalytic reduction (SCR) using CO, NH$_3$ and thermal degradation have been used. Because of the toxic nature of CO and its presence in most of NOx containing streams, simultaneous removal of CO and NO using catalytic reduction seems to be an ideal strategy for the removal of these two pollutants. Noble metal and perovskite type oxides are catalysts which used for NO + CO reaction $^{1,2}$, being noble metals more active than perovskites but also much more expensive.

Perovskite type oxides are mixed oxides with nominal formulation of ABO$_3$ or A$_2$BO$_4$ where A is a larger cation than B. When perovskite are used as catalysts, B usually designates a transition metal cation surrounded by six oxygen in octahedral coordination, and A is a cation of rare-earth metal coordinated by 12 oxygens $^3$. Many metals are stable through the perovskite structure which provides that the A and B cations have dimension ($r_A > 0.90$ Å, $r_B > 0.51$ Å) in agreement with the limits of the so-called “tolerance factor” t ($0.8 < t < 1.0$), defined by Goldschimdt as
t = (r_A + r_O)/\sqrt{2}(r_B + r_O), and where r_A, r_B and r_O are the ionic radii for A, B and O, respectively. Properties of perovskite type oxides are mainly depend on nature of A and B cations. In fact, A cations are responsible of the structure stability of perovskite, and B cation determines the catalytic activity. Potentially, A and/or B cation could be replaced by other A' and B' foreign cations without destruction of matrix structure. According to the findings, such a modification leads to structural defects and oxygen excess or oxygen deficiency that are favorable for catalytic activity.

The perovskite type oxides were used in many catalytic processes including catalytic combustion or deep oxidation of volatile organic compounds (VOC’s), CO oxidation, syngas production, among other catalytic reactions. As for other catalytic reactions, nature of catalyst plays the main role in the success of CO + NO reaction. Many researchers studied NO removal by using perovskites as catalyst. Substitution of A and B site for Fe and Cu perovskites by other transition metals, and their catalytic performance for NO reduction by CO was tested. He et al. studied the substitution of Mn by Cu and Ag in a La_{0.8}Ce_{0.2}B_{0.4}Mn_{0.6}O_3 (B: Cu and Ag) perovskite catalyst for CO + NO reaction and concluded that Cu is more effective than Ag. The study of the use of various metals in A site, including La, Nd, Sm carried out by Ciambelli et al., showed the following sequence of catalyst activity: La>Nd>Sm. The impacts and effects of the modification of the perovskite formulations by Pd were also studied, concluding that it is an effective element for improving the catalytic activity of perovskites. Thus, the aim of this work is to compare the catalytic performance of perovskites with various transition metals in B site and to analyze the effect of modification of the best formulation to increase the catalytic activity. Therefore, catalysts with various formulation of LaBO_3 or La_2BO_4 (B: Mn, Fe, Co, Ni, Cu, Zn) were synthesized by citric acid method and tested for simultaneous removing of the NO + CO, while the most active catalyst has been selected and modified by using other transition metals in order to improve the catalytic performance. Synthesized catalysts have been characterized by using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), Temperature Programed Reduction with hydrogen (H_2-TPR), X-ray Photoelectron Spectroscopy (XPS) and Scanning electron microscopy (SEM) to determine the physical-chemical properties affecting the catalytic performance.
Experimental

Catalyst preparation
The sol-gel method, as described elsewhere \(^6\), was used to obtain the catalysts. Briefly, stoichiometric amounts of metal nitrates precursor (La(NO\(_3\))\(_3\).6H\(_2\)O, Mn(NO\(_3\))\(_2\).4H\(_2\)O, Fe(NO\(_3\))\(_3\).9H\(_2\)O, Co(NO\(_3\))\(_2\).6H\(_2\)O, Ni(NO\(_3\))\(_2\).6H\(_2\)O, Cu(NO\(_3\))\(_2\).3H\(_2\)O, Zn(NO\(_3\))\(_2\).6H\(_2\)O) were dissolved using the minimum amount of distilled water to get a clear solution (Sol). The solution was heated till 70\(^\circ\) C on a hot plate and then an appropriate amount of the citric acid monohydrate was added (As proposed in our previous work \(^6\), the molar ratio of citric acid to the total nitrates in the solution mixture was kept at 0.525.) The mentioned solution was stirred vigorously and heated to 80\(^\circ\)C for dehydration and, finally, a sticky gel was obtained which was burned by heating at 200 \(^\circ\)C on a hot plate and turned into a dark powder. The powder was calcined in two steps: at 500\(^\circ\)C for 1 hour, and, then, at 700\(^\circ\)C for 5 hours.

Catalyst characterization
The determination of crystalline phases was carried out using X-ray diffraction on a SIEMENS D500 diffractometer and Cu K\(_\alpha\) radiation (\(\lambda = 1.54\) \(\text{\AA}\)). Diffractograms were recorded with a step of 4\(^\circ\) per minute for \(2\theta\) between 20 and 80\(^\circ\). The ICSD standards were utilized as patterns for the identification of phases in the diffractograms. The particle sizes (D) were evaluated by means of the Scherrer equation (D = K\(\lambda\)/\(\beta\ cos \theta\)), where K is a constant equal to 0.89, \(\lambda\) is the wavelength of the X-ray and \(\beta\) is the effective line width of the X-ray reflexion).

A Chembet-3000 apparatus was used for the H\(_2\)-TPR experiments, and that were carried out under a 10 mL.min\(^{-1}\) flow of 5% H\(_2\) in Ar, using a heating 10 \(^\circ\)C.min\(^{-1}\) up to 1000 \(^\circ\)C.

The BET surface area (m\(^2\)/g) was analyzed and determined by N\(_2\) adsorption at 77 K by using an F-Sorb 3400 volumetric adsorption/desorption apparatus. Prior to measurement, the samples were degassed at 150 \(^\circ\)C under vacuum for 3 hours.

The surface composition and elemental chemical state of the samples were examined by XPS, using a Model VG ESCALAB apparatus with AlK\(_\alpha\) X-ray source. The binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV).
Finally, the surface morphology was determined by SEM using a Hitachi S3000N electron microscope (JEOL, Japan).

**Catalytic studies**

Figure 1 shows a simple scheme of catalytic set-up used. The CO + NO reaction was carried out in a straight quartz reactor (l = 2 cm, i.d. = 0.8 cm, where the 200 mg catalyst was inserted between two quartz wool plugs) at different temperatures under atmospheric pressure. Before reaction tests, the catalysts should be pretreated with air (40 cm$^3$ min$^{-1}$) at 300°C for 2 hours. The total flow rate was 200 cm$^3$ min$^{-1}$ and the gas composition was 3000 ppm NO and 3000 ppm CO balanced with Ar. Gas hourly space velocity (GHSV) was fixed about 12000 h$^{-1}$ and the reaction temperature was controlled by using K-type thermocouple.

A Shimadzu 2010 gas chromatograph (GC), equipped with a TCD detector and a HP-Molesieve (Agilent, USA) column (l = 30 m, i.d. = 0.53 mm) with helium as carrier gas, was used to analyze the feed and product gases.

![Figure 1: Simple scheme of catalytic test set up for CO+NO reaction.](image)
Results

Catalysts characterization

The XRD results of LaBO$_3$ (B: Mn, Fe, Co, Ni) and La$_2$CuO$_4$ catalysts were presented in Figure 2 and, as it is possible to be seen, the XRD pattern of LaMnO$_3$, LaFeO$_3$, LaCoO$_3$, LaNiO$_3$ and La$_2$CuO$_4$ catalysts are in agreement with standard patterns ICSD 082315, ICSD 084941, ICSD 201763, ICSD 067717 and ICSD 019003, respectively. La$_2$CuO$_4$ XRD pattern shows the presence of some CuO (at 2θ about 39 and 35).

![Figure 2: XRD results of LaBO$_3$ B (Mn, Fe, Co, Ni) and La$_2$CuO$_4$ catalysts](image)

The Figure 3 shows XRD patterns of modified LaFeO$_3$ catalysts compared with that of the pure LaFeO$_3$ to feature the effect of the incorporation of the modifier metals in the structure of...
LaFeO₃. Thus, the structure of LaFe₀.₇M₀.₃O₃ (M: Mn, Co and Cu) is similar to LaFeO₃ itself and, consequently, it can be concluded that there is not any second metal oxide phase in the catalyst structure. Figure 3b, where a comparison of the catalysts main peak is shown, reveals a shift due to the metals insertion in the LaFeO₃ structure. The change of the unit cell size shown in table 1 proves that the metals were inserted into the LaFeO₃ crystalline structure and did not form a second crystalline phase.
Figure 3: XRD patterns of modified LaFeO\textsubscript{3} catalysts compared with pure LaFeO\textsubscript{3} (a) and 2\(\Theta\) shift for different metals as modifier (b).

Table 1: Unit cell parameters and cell volume for LaFeO\textsubscript{3} catalyst before and after modification by other transition metals.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeO\textsubscript{3}</td>
<td>5.56</td>
<td>5.56</td>
<td>7.89</td>
<td>243.90</td>
</tr>
<tr>
<td>LaFe\textsubscript{0.7}Cu\textsubscript{0.3}O\textsubscript{3}</td>
<td>5.54</td>
<td>5.54</td>
<td>7.86</td>
<td>241.66</td>
</tr>
<tr>
<td>LaFe\textsubscript{0.7}Mn\textsubscript{0.3}O\textsubscript{3}</td>
<td>5.52</td>
<td>5.53</td>
<td>7.83</td>
<td>238.92</td>
</tr>
<tr>
<td>LaFe\textsubscript{0.7}Co\textsubscript{0.3}O\textsubscript{3}</td>
<td>5.51</td>
<td>5.52</td>
<td>7.81</td>
<td>237.81</td>
</tr>
</tbody>
</table>

XPS studies

The surface composition of LaFeO\textsubscript{3}, LaMnO\textsubscript{3} and LaFe\textsubscript{0.7}Mn\textsubscript{0.3}O\textsubscript{3} catalysts was determined. In Figure 4, XPS spectra of 2\(p_{3/2}\) area for Fe in LaFeO\textsubscript{3} (a), Mn in LaMnO\textsubscript{3} (b), Fe in LaFe\textsubscript{0.7}Mn\textsubscript{0.3}O\textsubscript{3} (c) and Mn in LaFe\textsubscript{0.7}Mn\textsubscript{0.3}O\textsubscript{3} can be seen. In Figure 4, peaks on about 710 ev, 713 ev, 641 ev and 644 ev are assigned to Fe(III), Fe(IV), Mn(III) and Mn(IV), respectively.
Figure 4: XPS spectra of 2p$^{3/2}$ area for Fe in LaFeO$_3$ (a), Mn in LaMnO$_3$ (b), Fe in LaFe$_{0.7}$Mn$_{0.3}$O$_3$ (c) and Mn in LaFe$_{0.7}$Mn$_{0.3}$O$_3$.

In Figure 5, the XPS spectra of 1s area for oxygen in LaFeO$_3$, LaMnO$_3$ and LaFe$_{0.7}$Mn$_{0.3}$O$_3$ are presented. In the three spectra, the first peak around the 529 ev corresponds to lattice oxygen, the second peak around the 531.5 ev is assigned to surface oxygen and the third peak at about 533.5 ev belongs to adsorbed water.
**Figure 5**: XPS spectra of O 1s area for oxygen in LaFeO$_3$, LaMnO$_3$ and LaFe$_{0.7}$Mn$_{0.3}$O$_3$

**BET results**

Surface area of catalysts were shown in table 2. LaMnO$_3$ shows the highest surface area and LaFe$_{0.7}$Mn$_{0.3}$O$_3$ the lowest one. The LaFe$_{0.7}$Mn$_{0.3}$O$_3$ presents a surface area in between the two raw peovskite.

**Table 2**: Surface area of LaFeO$_3$, LaMnO$_3$ and LaFe$_{0.7}$Mn$_{0.3}$O$_3$

<table>
<thead>
<tr>
<th>Catalyst Number</th>
<th>Catalyst Formulation</th>
<th>BET (m$^2$/gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LaFeO$_3$</td>
<td>7.8</td>
</tr>
<tr>
<td>2</td>
<td>LaMnO$_3$</td>
<td>40.5</td>
</tr>
<tr>
<td>3</td>
<td>LaCoO$_3$</td>
<td>25.7</td>
</tr>
<tr>
<td>4</td>
<td>LaFe$<em>{0.7}$Co$</em>{0.3}$O$_3$</td>
<td>18.9</td>
</tr>
<tr>
<td>5</td>
<td>LaFe$<em>{0.7}$Cu$</em>{0.3}$O$_3$</td>
<td>17.71</td>
</tr>
<tr>
<td>6</td>
<td>LaFe$<em>{0.7}$Mn$</em>{0.3}$O$_3$</td>
<td>32.3</td>
</tr>
</tbody>
</table>

**SEM analysis**

Figure 6 presents the SEM images of the catalysts where a defined morphology is not observed.
The reducible active sites of each catalyst were analyzed by using H$_2$- TPR method, and the results are shown in Figure 7. The TPR profile for LaFeO$_3$ shows two significant peaks starting from 410°C which can be assigned to the reduction of Fe(IV) and Fe(III), respectively. In addition, two significant peaks were revealed for LaMnO$_3$ related to the reduction of Mn(IV) and Mn(III) starting from about 200°C and 700°C.
For LaFe_{0.7}Mn_{0.3}O_3, the H_2-TPR profile change significantly and two significant peaks were observed; first peak starting from about 330°C can be assigned to the reduction of Mn(IV) and the second peak was a possible mixture of peaks related to the reduction of Fe(IV), Fe(III) and Mn(III). Additionally, it is clear from Figure 7 that the amount of reducible active sites for LaFe_{0.7}Mn_{0.3}O_3 was significantly increased respect to LaFeO_3 catalyst.

**Catalytic activity for CO + NO removal**

The catalytic performance of catalysts is shown in Figure 8, where it is observed that, as expected, the NO and CO conversion increased with the reaction temperature for all catalysts. The difference between catalytic activities increased with the reaction temperature, being the largest at 400°C. At this temperature, the sequence of activity was LaFeO_3 > LaCoO_3 > La_2CuO_4 > LaNiO_3 > LaMnO_3 > LaZnO_3, so, LaFeO_3 is the most active catalyst.
Figure 8: Catalytic activity of LaBO₃ (B: Mn, Fe, Co, Ni and Zn) and La₂CuO₄ for NO reduction by CO.
For CO + NO reaction, the N$_2$ is the desired product being N$_2$O an intermediate and undesired product due its greenhouse effect (10 times larger than that of the CO). In Figure 9, N$_2$O and N$_2$ yield of catalysts versus reaction temperature is shown.

Figure 9: N$_2$O and N$_2$ of yield LaBO$_3$ (B: Mn, Fe, Co, Ni and Zn) and La$_2$CuO$_4$ catalysts.
The N₂O yield shows a volcano type behavior and the maximum in the N₂O yield is reached for each catalyst at different reaction temperatures. The yield of N₂O is higher for the more active catalysts including LaFeO₃ and LaCoO₃ because of the higher NO conversion. The maximum N₂O yield is about 5% at 300°C for the most active catalyst (LaFeO₃) and decreased by increasing reaction temperature reaching zero at 500°C approximately. Based on results of Figure 8 and 9, the LaFeO₃ is the most active catalyst with 100% N₂ yield at high reaction temperatures and, therefore, this formulation has been selected to be modified (LaFe₀.₇M₀.₃O₃, being M: Mn, Co and Cu) using other active transition metals ⁶⁻⁸.

In Figure 10, the NO, CO conversion, N₂O yield and N₂ yield for the LaFe₀.₇M₀.₃O₃ catalyst is shown. It is observed that the addition of Mn increased catalyst activity significantly, while addition of Cu and Co has not a significant effect at low temperatures and even resulted in a decrease of the activity at high reaction temperatures.Besides, from Figure 10.b it is deduced that addition of Mn, increases the N₂O selectivity at low temperature, however, the N₂O selectivity is acceptable and reaches zero at high temperatures.

![Graph showing NO and CO conversion for different catalysts as a function of reaction temperature.](image-url)
The modification of LaFeO$_3$ by Mn resulted in an enhancement in catalytic activity for NO + CO reaction. Based on results which were presented in Figure 3, the LaFe$_{0.7}$Mn$_{0.3}$O$_3$ catalyst has the similar crystal structure to LaFeO$_3$ which means that the modifier metal (Mn) were not incorporated in any other metal oxide phase except the LaFe$_{0.7}$Mn$_{0.3}$O$_3$. Also, slight shifts on XRD peaks of LaFe$_{0.7}$Mn$_{0.3}$O$_3$ in comparison to LaFeO$_3$, is a result of unit cell size change (table 2) which happened because of Mn insertion into the LaFeO$_3$ crystal structure. From Figure 4 and based on XPS analysis, it is deduced that the surface amount of Mn(IV) was increased for LaFe$_{0.7}$Mn$_{0.3}$O$_3$ respect to LaMnO$_3$, this is because after incorporation of Mn in LaFeO$_3$ structure, the ratio of Mn(IV) to Mn(III) increased from 0.373 to 0.694 for LaFe$_{0.7}$Mn$_{0.3}$O$_3$. In fact, the simultaneous use of Mn with other transition metals as B ion leads to an increase in Mn(IV) to Mn(III) ratio. From the stoichiometric point of view, the Mn should be in Mn(III) state to achieve the neutral compound. As consequence of the change from Mn (III) to Mn (IV),
structural defects should be created to maintain the compound neutrality. Thus, the structural defects can be seen as an increase of surface oxygen vacancies as a result of the high Mn(IV) concentration in composition. On the other hand, the ratio of Fe(IV) to Fe(III) is 0.665 and 0.644 for LaFeO$_3$ and LaFe$_{0.7}$Mn$_{0.3}$O$_3$, respectively, so, it is almost constant. In addition, based on the peaks area on Figure 5, the surface oxygen to lattice oxygen ratio is 0.301, 0.673 and 0.408 for LaFe$_{0.7}$Mn$_{0.3}$O$_3$, LaFeO$_3$ and LaMnO$_3$, respectively. Thus, the lower surface oxygen to lattice oxygen ratio of LaFe$_{0.7}$Mn$_{0.3}$O$_3$ confirms the larger amount of vacancies structural defects created. According to the mechanism established for CO + NO reaction $^{20, 24}$ by increasing the vacancies, the surface adsorption of the NO and CO reactants was facilitated and, as a result, the catalytic activity was improved $^{24, 25}$. Besides, it is clear from H$_2$-TPR results (Figure 7) that the amount of reducible active sites for LaFe$_{0.7}$Mn$_{0.3}$O$_3$ catalyst was significantly increased respect to LaFeO$_3$ catalyst. This is because the area of reduction peak about 600°C of LaFe$_{0.7}$Mn$_{0.3}$O$_3$ is significantly larger respect to the same peak for LaFeO$_3$. Since NO + CO is an oxidation/reduction reaction; the number of reducible active sites plays an important role. Thus, H$_2$-TPR results are also in agreement with XPS analysis.

On the other hand, the LaFe$_{0.7}$Mn$_{0.3}$O$_3$ presents a surface area in between the two raw perovskites. This indicates that surface area cannot be the determining parameter for activity of synthesized catalysts. Also, there is not any significant change in the surface area of the synthesized catalysts before and after the modification. Moreover, SEM results are also in agreement with BET results as any specific surface morphology was not observed for synthesized catalysts.

Therefore, the enhancement in Mn(IV) to Mn(III) ratio, an increase in amount of surface vacancies and on the reducible sites, are the key parameters determining the catalytic activity.

**Conclusion**

In the present study, different perovskite formulations, including La and a series of transition metals Mn, Fe, Co, Ni, Cu and Zn, were synthesized by using citrate method and tested in CO+NO reaction. LaFeO$_3$ was selected for modification by using Mn, Co and Cu because its superior activity in comparison to other formulations. The catalytic activity of LaFeO$_3$ which was modified by Mn (LaFe$_{0.7}$Mn$_{0.3}$O$_3$) was increased significantly. The XRD analysis proved the
perovskite structure for catalysts and the insertion of modifier metals into the crystal structure of LaFeO$_3$. The XPS analysis revealed that the increase of Mn (IV) to Mn (III) ratio, resulting in the enhancement of the structural defects. The mentioned defects increased the reducible active sites of LaFe$_{0.7}$M$_{0.3}$O$_3$ catalyst and, as a consequence, the catalytic activity for NO+CO reaction, which is an oxidation/reduction reaction, is improved.

**Acknowledgement**

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**References**

1. Belessi, V.; Trikalitis, P.; Ladavos, A.; Bakas, T.; Pomonis, P. Structure and Catalytic Activity of La$_{1-x}$FeO$_3$ System (x=0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.35) for the NO+CO Reaction. *App. Catal. A: Gen.* 1999, 177 (1), 53.


7. Hosseini, S. A.; Salari, D.; Niaei, A.; Oskoui, S. A. Physical–Chemical Property and Activity Evaluation of LaB$_{0.5}$Co$_{0.5}$O$_3$ (B= Cr, Mn, Cu) and LaMn$_x$Co$_{1-x}$O$_3$ (x= 0.1, 0.25, 0.5) Nano Perovskites in VOC Combustion. *J. Ind. Eng. Chem.* 2013, 19, 1903.


(13) Wang, H.; Cong, Y.; Yang, W. Investigation on the Partial Oxidation of Methane to Syngas in a Tubular Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3 Membrane Reactor. *Catal. Today.* **2003**, *82*, 157.


(18) He, H.; Liu, M.; Dai, H.; Qiu, W.; Zi, X. An Investigation of NO/CO Reaction over Perovskite-type Oxide La_{0.8}Ce_{0.2}B_{0.4}Mn_{0.6}O_{3} (B= Cu or Ag) Catalysts Synthesized by Reverse Microemulsion. *Catal. Today*. **2007**, *126*, 290.


(22) Magalhães, F.; Moura, F. C. C.; Ardisson, J. D.; Lago, R. M. LaMn_{1-x}Fe_xO_3 and LaMn_{0.1-x}Fe_{0.9}Mo_{2}O_3 Perovskites: Synthesis, Characterization and Catalytic Activity in H_2O_2 Reactions. *Mat. Res.* **2008**, *11*, 307.


(24) Leontiou, A.; Ladavos, A.; Pomonis, P. Catalytic NO Reduction with CO on La_{1-x}Sr_{x}(Fe^{3+}/Fe^{4+})O_{3+x+y} Perovskite-type Mixed Oxides (x = 0.00, 0.15, 0.30, 0.40, 0.60, 0.70, 0.80, and 0.90). *App. Catal. A: Gen.* **2013**, *241*, 133.


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