

Synthesis, Characterization, and Catalytic Activity of Nanocrystalline $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ during the Combustion of Toluene

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Abstract: Nanostructured LaFeO_3 and substituted $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0.1, 0.15, \text{ and } 0.2$) perovskites were synthesized by sol-gel auto-combustion and their activities during the combustion of toluene were evaluated. The structure and physico-chemical properties of the perovskites were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and BET surface area analyses. The compounds were crystallized as a perovskite phase with an orthorhombic structure. The mean particle size of the perovskites increased with an increase in europium loading while the specific surface area decreased. Characterization data confirmed that a total insertion of Eu into LaFeO_3 occurred at $x \leq 0.15$. However, Eu_2O_3 segregation occurred to some extent especially at $x > 0.15$. The catalytic activity of the catalysts increased substantially with an increase in Eu substitution in the evaluated range.

Key words: perovskite; sol-gel; europium; volatile organic compounds; catalytic oxidation

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One of the reasons for the formation of photochemical smog is the reaction between volatile organic compounds (VOCs) and nitrogen oxides in the presence of sunlight [1]. Automobiles and industrial processes are mainly responsible for VOC emissions. VOCs such as hydrocarbons, alcohols, ketones, and aldehydes [2,3] are readily oxidized. When the recovery of these compounds is not desired they are usually destroyed by deep oxidation. Catalytic combustion is regarded as an effective and economic way to control air pollution [4]. The catalysts currently used for environmental purposes are either noble metals or metal oxides. Although noble metals are the most active and effective catalysts for VOC decomposition they have a high sintering rate and are expensive [5]. Transition metal perovskites are known to be very good oxidation catalysts [6]. Previous studies have evaluated perovskites for VOCs combustion. In our previously work we studied the activities of $\text{LaZn}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.01, 0.05, 0.1, 0.2, \text{ and } 0.3$) perovskites for the catalytic combustion of toluene [1]. Chang et al [7] found that $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ was highly active for the remediation of toluene and methyl ethyl ketone. The combustion of some VOCs on LaMnO_3 has been reported by Lintz and Wittstock [8]. Arai et al [9] found a very high activity for the deep combustion of methane with Sr-doped LaMnO_3 . At conversion levels below 80%, Sr-doped LaMnO_3 was more active than $\text{Pt/Al}_2\text{O}_3$. McCarty and Wise reported the high

oxidation activities of $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3+x}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ [10]. They found that a correlation exists between VOCs oxidation rate and the bond dissociation energy of the weakest C–H bond [11,12]. The substitution of lanthanides instead of lanthanum in perovskites is promising for these catalysts. Costa and Santos reported Mössbauer studies of $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ [13].

The aims of this work are the synthesis of europium doped LaFeO_3 perovskites by sol gel auto-combustion and the study of $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ nanocatalysts during the combustion of volatile organic compounds to explore the effect of Eu loading on the catalytic activity of the nanocatalysts. Toluene is considered to represent the aromatic VOCs that are commonly used in industry. The catalysts were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and N_2 adsorption.

1 Experimental

1.1 Preparation

For the preparation $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ perovskites $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Eu_2O_3 and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (citric acid) were used as starting materials and they were analytical grade (Merck). The required quantity of Eu_2O_3

was dissolved in a minimum amount of nitric acid to form Europium nitrate and this was mixed with specific amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and a citric acid solution to form the sol. The molar amount of citric acid was equal to the total molar amount of metal nitrates in solution. The solution was evaporated by vigorous stirring at 80 °C for 2 h then by gradually increasing the temperature to 100 °C the slurry burned and transformed into a brown powder. The brown powder obtained was calcined at 600 °C for 1 h and subsequently at 800 °C for 3 h.

1.2 Characterization

XRD measurements were carried out using a D500 Siemens with a $\text{Cu } K_\alpha$ line at a wavelength $\lambda = 0.154$ nm and at a scanning rate of 2°/min while the 2θ range was 4° to 70°. The FT-IR transmission spectra were recorded between 400 and 4000 cm^{-1} for all the samples using a FT-IR Tensor 27 (Bruker) by the KBr pellet technique. SEM images were obtained using a Joel JEM-100 CXII microscope.

1.3 Catalytic activity

The catalytic performance of the samples was evaluated by the combustion of toluene in a glass tube (i.d. = 0.8 cm) that was placed in an electric furnace while working under atmospheric pressure. In each run, 0.2 g of the catalyst was used for the catalytic tests. The hourly gas flow space velocity (GHSV) was 5000 h^{-1} and the reaction temperature ranged from 150 to 400 °C. The reactants and products were analyzed by gas chromatography (Shimadzu 2010, equipped with a flame ionization detector (FID)). The conversion rate was obtained by calculating the concentrations of the reactants (in the inlet and outlet of the reactor) at different temperatures.

2 Results and discussion

2.1 XRD results

The intensive peaks at a 2θ of 23.1°, 32.7°, 47.0°, and 58.9° represent the main features of the perovskite materials (by comparison with standard perovskite patterns) [14].

The XRD patterns of the samples show that it is a single phase of $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ with an orthorhombic ABO_3 perovskite structure. Figure 1 shows that the $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0, 0.1, \text{ and } 0.15$) samples are single phase perovskite-type oxides. By comparing the XRD patterns of $\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$ with LaFeO_3 shows that for $x > 0.15$ line broadening and a decrease in peak intensity is apparent, which corresponds to a decrease in the relative crystallinity of the perovskites. Additionally, for $\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$ the presence of small peaks

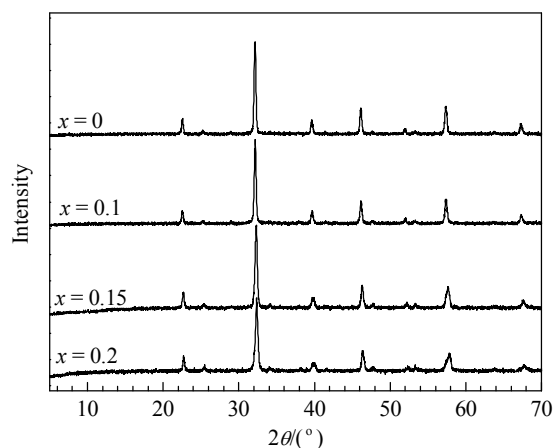


Fig. 1. XRD patterns of $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ and Eu_2O_3 .

at $2\theta = 20.3^\circ, 28.47^\circ, 32.99^\circ, 47.35^\circ,$ and 56.18° indicates the segregation of Eu_2O_3 [15]. Furthermore, a shift to higher 2θ was observed for the Eu doped perovskites, which is due to a change in the d-spacing. According to the peaks and the Scherrer formula [16] the diameters of the crystalline particles of the perovskites were calculated between 20–40 nm for a 2θ of 23.1° [14]. We observed that the particle sizes increase with an increase in the amount of europium loading, which replaces the lanthanum in the A sites of the perovskite lattice. The results are in agreement with the results of Huang et al. who investigated $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [14]. Furthermore, the particle size was found to increase with an increase in the calcination temperature.

2.2 FT-IR measurements

IR spectra of the nanocrystalline $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0, 0.1, 0.15,$ and 0.2) perovskite synthesized powder samples are shown in Fig. 2. The IR peaks at about 400 and 560 cm^{-1} are closely related to the bending vibration of O–Fe–O and the stretching vibration of Fe–O, respectively. In addition, a

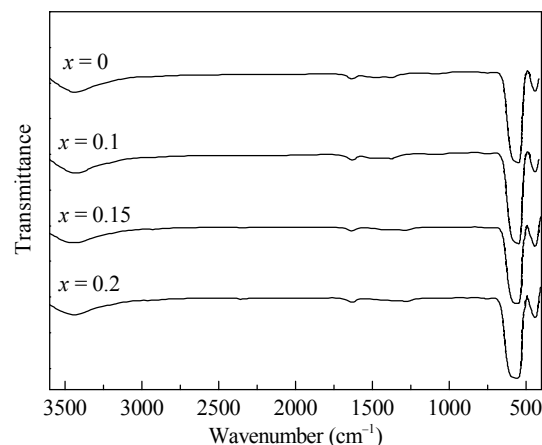


Fig. 2. FT-IR spectra of the $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ perovskites.

broad band appeared at around 3600 cm^{-1} , which is attributed to the stretching vibration of O–H in the adsorbed water molecules from the moisture in the KBr that was used to prepare the pellets [17]. However, with an increase in the Eu doping content the frequency of the IR absorption peak at 400 and 560 cm^{-1} shifted slightly to a higher frequency for the $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ systems. The shift in bands corresponds to the presence of Eu–O bonds in the compounds.

2.3 SEM micrographs

Figure 3 shows SEM micrographs of the LaFeO_3 and $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0.1, 0.15, \text{ and } 0.2$) compounds. The average particles of the perovskites are small ($\leq 100\text{ nm}$) and they are similar in size. The particles are distributed uniformly and the mean particle sizes are less than 50 nm , which is in good agreement with results obtained by XRD.

The BET specific surface areas of these samples are summarized in Table 1. The largest BET surface area ($30.1\text{ m}^2/\text{g}$) was obtained for the LaFeO_3 perovskite. The partial substitution of La by Eu caused a progressive decrease in the BET surface area and the lowest value ($27.7\text{ m}^2/\text{g}$) was obtained for $\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$.

2.4 Catalytic activity of the perovskites

The thermal combustion of toluene at different temperatures was performed under the same conditions. The maximum conversion of toluene was obtained at $400\text{ }^\circ\text{C}$ (35%). In a control test, toluene was not oxidized at temperatures below $150\text{ }^\circ\text{C}$. The activities of the catalysts for the total oxidation of toluene were also evaluated. The activities of

Table 1 BET specific surface areas of the $\text{LaZn}_n\text{Fe}_{1-x}\text{O}_3$ perovskites

Perovskite	$S_{\text{BET}}/(\text{m}^2/\text{g})$
LaFeO_3	30.1
$\text{La}_{0.9}\text{Eu}_{0.1}\text{FeO}_3$	28.9
$\text{La}_{0.85}\text{Eu}_{0.15}\text{FeO}_3$	28.4
$\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$	27.7

LaFeO_3 and $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0.1, 0.15, \text{ and } 0.2$) during the oxidation of toluene are shown in Fig. 4. The catalysts apparently lowered the activation energy for the oxidation of toluene and lower initial burning temperatures were required. We observed that compared to LaFeO_3 the $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ catalysts gave better activity for the oxidation of toluene.

Figure 4 shows that the conversion of toluene over the catalysts increased as the Eu loading increased and $\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$ gave the highest activity at a defined temperature in the tested range. The ignition temperature $T_{50\%}$, defined as the temperature required to reach 50% conversion for toluene, for the catalysts is shown in Table 2. The $T_{50\%}$ for toluene decreased with an increase in Eu insertion. Considering both the reaction temperature and the conversion rate (Table 2, Fig. 4), it is obvious that the activities of $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ are higher than that of LaFeO_3 under the same conditions during the total combustion of toluene. These catalysts were prepared by the partial substitution of europium (Eu) for lanthanum (La) at the A-sites of LaFeO_3 . The substitution modifies the surface structure of the catalyst by greatly increasing the oxygen vacancies in the surface regions, which results in higher catalytic activities for $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ compared to LaFeO_3 .

The insertion of europium increased the amount of sur-

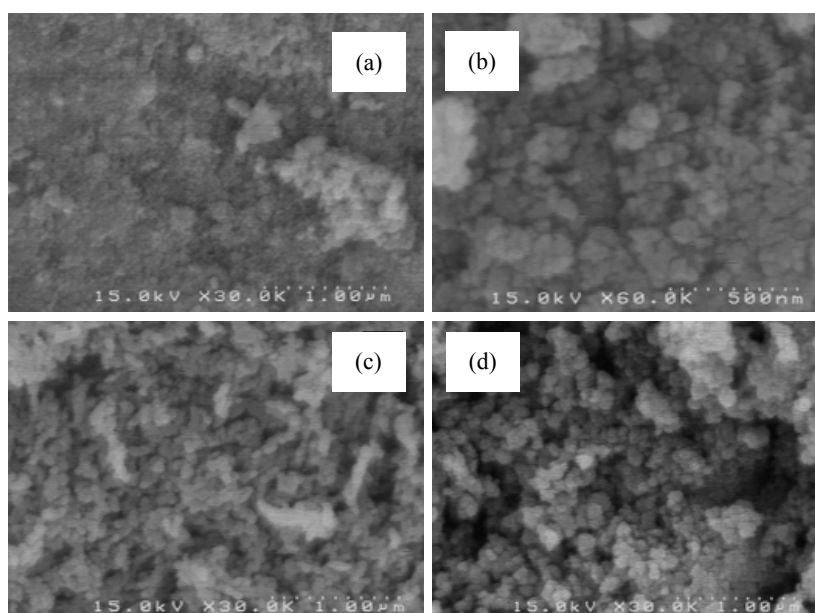


Fig. 3. SEM images of LaFeO_3 (a), $\text{La}_{0.9}\text{Eu}_{0.1}\text{FeO}_3$ (b), $\text{La}_{0.85}\text{Eu}_{0.15}\text{FeO}_3$ (c), and $\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$ (d).

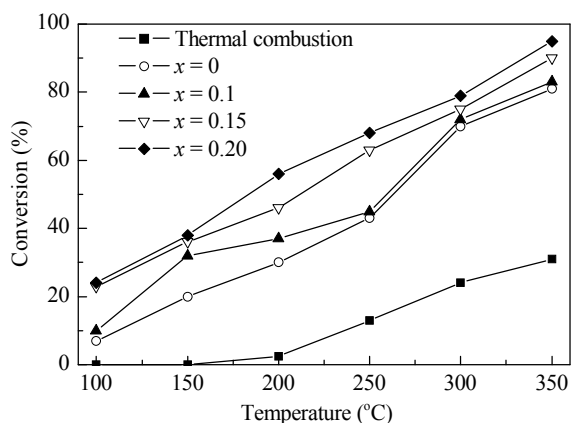


Fig. 4. Conversion of toluene with LaFeO_3 and $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ nanocatalysts.

Table 2 Reaction temperatures for 50% toluene conversion over the catalysts

Catalyst	$T_{50\%}/^\circ\text{C}$
LaFeO_3	268
$\text{La}_{0.9}\text{Eu}_{0.1}\text{FeO}_3$	259
$\text{La}_{0.85}\text{Eu}_{0.15}\text{FeO}_3$	212
$\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$	183

face oxygen on the perovskites. Toluene reacts with surface oxygen by the ‘suprafacial’ reaction mechanism, as proposed by Voohoeve and co-workers [18]. This mechanism comes from the interaction between the reactants and surface oxygen at low temperatures ($< 400^\circ\text{C}$). The amount of surface oxygen increases with an increase in Eu loading. Similar results were obtained for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and LaCoO_3 for the combustion of VOCs [14]. Furthermore, a correlation between the specific surface area (BET) and the activities reveal that the BET surface area is not a determining factor for the catalytic activity of $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ because $\text{La}_{0.8}\text{Eu}_{0.2}\text{FeO}_3$ with the lowest specific surface area gave the highest activity. This is consistency with the results of our previous research into $\text{LaZn}_{1-x}\text{Fe}_x\text{O}_3$ [1].

3 Conclusions

Nanocrystalline LaFeO_3 and $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0.1, 0.15, \text{ and } 0.2$) with a perovskite structure were successfully synthesized by the sol gel auto-combustion method. Single

perovskite phases are obtained when $x < 0.15$. Some segregation of Eu_2O_3 was obtained for substitutions higher than 0.15 ($x > 0.15$). The catalysts were tested for their catalytic activity during the oxidation of VOCs. $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ gave better activities compared to LaFeO_3 for the total combustion of toluene and the activities increased with an increase in Eu doping into $\text{La}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x \leq 0.2$) in the range that was evaluated.

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