Catalytic Oxidation of Toluene over LaBO$_3$ (B=Fe, Mn and Co) and LaCo$_{0.7}$B$'_{0.3}$O$_3$ (B$'$=Fe and Mn) Perovskite-type

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ARTICLE INFO	ABSTRACT
	In this paper, LaBO$_3$ perovskite-type catalysts were prepared by sol-gel auto combustion method. Activity of catalysts was tested in catalytic oxidation of toluene. LaCoO$_3$ showed the highest activity among LaBO$_3$ perovskite catalysts. So, this catalyst was selected for further investigation. LaBO$_3$ perovskite catalysts were modified by substitution of Co by Fe and Mn. The catalytic activity of LaCoO$_3$ improved due to partial substitution of Co by B cations. LaCo$_{0.7}$Mn$_{0.3}$O$_3$ showed the highest activity among the synthesized catalysts. The structures of synthesized perovskites were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. The results of X-ray diffraction indicated that the LaBO$_3$ and LaCo$_{0.7}$B$'_{0.3}$O$_3$ samples obtained using sol-gel method had a pure perovskite-type crystal structure.

1. Introduction

Catalytic oxidation of volatile organic compounds (VOCs) has been extensively investigated in recent decades. VOCs are generally produced and released from the combustion process of fossil fuel [1]. Toluene is a common VOC used as raw material in manufacturing and also used as a solvent in the processes of several industries. Catalytic oxidation is one of the most efficient techniques for the removal of VOCs [2, 3]. Supported noble metal catalysts have excellent low temperature activities, but high costs limit their application. Perovskite type oxide catalysts are alternatives for supported noble metal catalysts because of their lower cost and good formulation flexibility which help researchers to formulate high activity catalysts [4, 5].

Perovskite-type oxides of general formula ABO$_3$ have been investigated extensively for their physical and catalytic properties [6]. A is usually lanthanide and B is usually the first row transition metals ion [7, 8]. Both A and B cations can be partially substituted, leading to substituted compounds with a general formula

$(A_{1-x}A'_xB_{1-y}B'_yO_3)$ [9, 10].

Niu et al. [11] prepared $La_{1-x}Sr_xMO_{3-\delta}$ (M=Co, Mn; x=0, 0.4) perovskite-type oxides using the citric acid complexing-hydrothermal-coupled method. $LaMO_3$ has better activity than $La_{0.6}Sr_{0.4}MO_3$. Huang et al. [12] investigated the effects of Sr on $LaCoO_3$ perovskites for VOCs oxidation. They found $La_{0.8}Sr_{0.2}CoO_3$ had much higher activity than $LaCoO_3$. Levasseur et al. [13] studied $La_{1-y}Ce_yCo_{1-x}Fe_xO_3$ Perovskite-type mixed oxides for CH_3OH, CO and CH_4 oxidation. They found the catalytic activity in VOC oxidation is enhanced by introduction of cerium in the A-site of perovskites. Oskoui et al. [9] investigated perovskite type oxide with $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ formula for toluene oxidation. They found high activity of the catalyst for toluene oxidation while mole fraction approaches around 0.9. Rousseau et al. [14] prepared $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ perovskites by sol–gel method. They found that the optimized composition was x=0.3 and y=0.2. Liu et al. [15] studied $La_{1-x}Ce_xMnO_3$ ($x = 0$–10 %) perovskite-type catalysts for catalytic oxidation of benzene which, in x=0.1, the perovskite catalysts show the highest activity. It should be mentioned that, all of the above mentioned optimization researches are based on catalytic activity.

In this paper, $LaBO_3$ and $LaCo_{0.7}B'_{0.3}O_3$ perovskite catalysts were synthesized by sol-gel auto combustion method and their activities were evaluated in catalytic oxidation of toluene. As mentioned before and based on our previous experiences, a combination of Co, Fe and Mn presents high catalytic activity for various oxidation reactions. Therefore, these transition metals are utilized for preparation of under study catalysts [7-15].

2. Experimental

$LaBO_3$ (B=Fe, Mn and CO) and $LaCo_{0.7}B'_{0.3}O_3$ (B′=Fe and Mn) perovskite samples were prepared by sol-gel auto combustion method using $La(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3.9H_2O$, $Mn(NO_3)_2.4H_2O$, $Co(NO_3)_2.6H_2O$ and citric acid (Merck) as precursors. The required amount of metal nitrates was dissolved in 50 mL deionized water. The obtained solution was mixed with appropriate quantity of citric acid aqueous solution. The molar ratio of citric acid to the total nitrate was 0.525, which was achieved in our previous work [9]. The obtained solution was heated to 80 ℃ under continuous stirring to evaporate the excess of the solvent until a sticky gel was obtained. In order to carry out gel decomposition, temperature was raised to 200 °C and finally the decomposed gel self-ignited and turned into a dark powder. Then, the powder was calcined for 5 h at 700 ℃. It should be mentioned that all of the synthesis parameters including molar ratios, calcination temperature and molar ratio of citric acid to the total nitrate have been optimized in our previous work [9].

Identification of crystalline phases was carried out using X-ray diffraction (XRD) on a SIEMENS D500 diffractometer (Germany) and Cu Kα radiation (λ=1.54 A). Diffractograms were recorded with a step of 0.25˚ per minute for 2θ between 20 and 80˚. The average crystal sizes of the perovskite using Scherer equation were according to Eq. (1).

$$d = \frac{K\lambda}{\beta\cos\theta}$$

(1)

Where d (nm) is the crystal size, θ is the Bragg angle, K is the constant of diffraction (0.89), λ (1.54056 nm) is the X-ray wavelength and β is the peak width at the half-maximum, corrected for instrument broadening.

The morphology of mixed oxides was determined via scanning electron microscopy (SEM) by TESCAN (Czech Republic) instrument. 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 °C under vacuum for 3 hours.

The activities of prepared catalysts were evaluated in a quartz tubular reactor (l=60 cm, i.d.=8 mm) at atmospheric pressure and at different temperatures (200-400 °C). 200 mg of the as-synthesized catalysts was placed in the middle of the reactor. Total flow rate of feed was 100 cm^3 min^{-1} (GHSV=6000 h^{-1}). The VOC-laden stream was generated at a fixed concentration by bubbling nitrogen gas at a suitable flow rate through the VOC saturator. The compositions of inlet and outlet gases were analyzed by an on-line gas chromatography (Shimadzu 2010) equipped with a flame ionization detector (FID) and CBP5 column (l=25 m, i.d.=0.25 mm). Schematic of experimental setup for toluene oxidation was shown in Fig. 1.
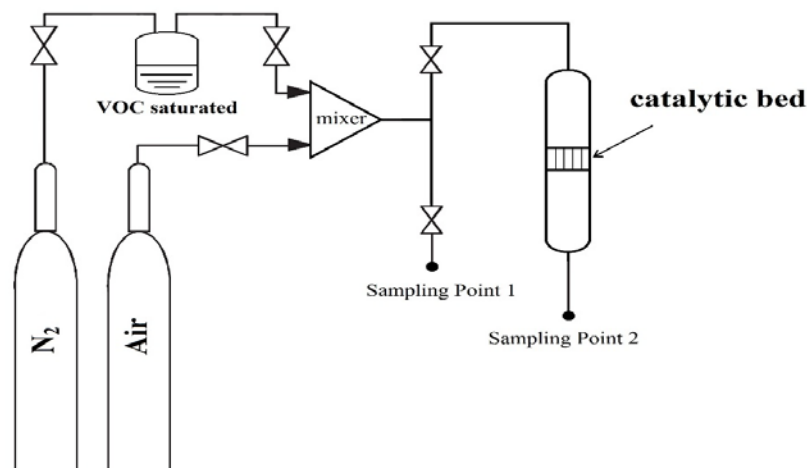

Figure 1. Schematic of toluene oxidation setup.

3. Results and discussion

The structure of catalysts with different composition was investigated using the X-ray diffraction method. XRD pattern for these catalysts is shown in Fig. 2. A comparison of XRD patterns with the pattern of LaFeO3 (ICDD 00-015-0148-PDF-2), LaMnO3 (ICDD 00-032-0484-PDF-2) and LaCoO3 (ICDD 00-006-0491-PDF-2) indicated that catalysts were single-phase perovskite oxides. Based on Scherer equation and XRD pattern, crystalline size of synthesized perovskites was calculated and summarized in Table 1. According to these calculations, size of catalysts crystals is below 30 nm.
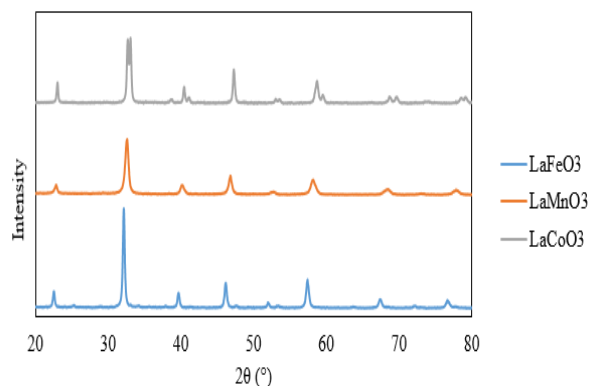
Figure 2. XRD patterns of $LaBO_3$ (B=Fe, Mn and Co).

Table 1
Mean crystalline size and BET surface area of $LaBO_3$ (B=Fe, Mn and Co).

Catalyst	Mean crystalline size	BET surface area
$LaFeO_3$	27	7.24
$LaMnO_3$	16	40.21
$LaCoO_3$	18	6.4

The morphology and particle size of synthesized perovskite catalysts were investigated by scanning electron microscopy (SEM). SEM images of perovskites are shown in Fig. 3. It is observed that the particle sizes are different for the samples.

Catalytic conversions of toluene over $LaBO_3$ (B=Fe, Mn and Co) are shown in Fig. 4. The temperature for 50 % and 100 % conversion of toluene (T50 % and T100 %) on $LaFeO_3$, $LaMnO_3$ and $LaCoO_3$ are listed in Table 2. By considering the T50 % and T100 % of toluene conversion as a criteria of activity, the following order was observed for performance of catalysts: $LaCoO_3 > LaFeO_3 > LaMnO_3$. Based on results, $LaCoO_3$ has the highest activity for toluene oxidation. So, $LaCoO_3$ was selected for further investigation. As can be seen, there is not any significant difference between morphology and surface area of various formulations. Therefore, the most important factor for catalyst activity is synergetic effect of metals in formulation.
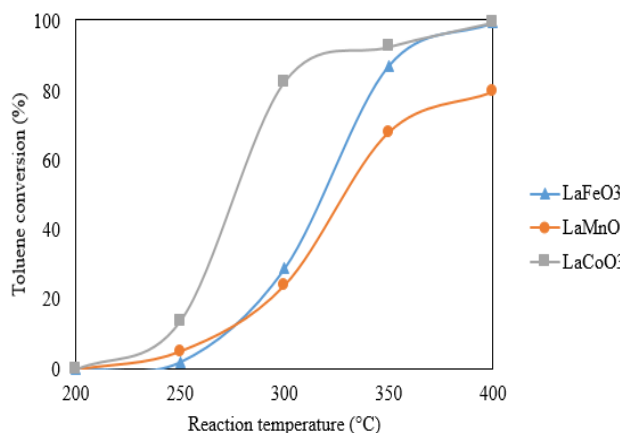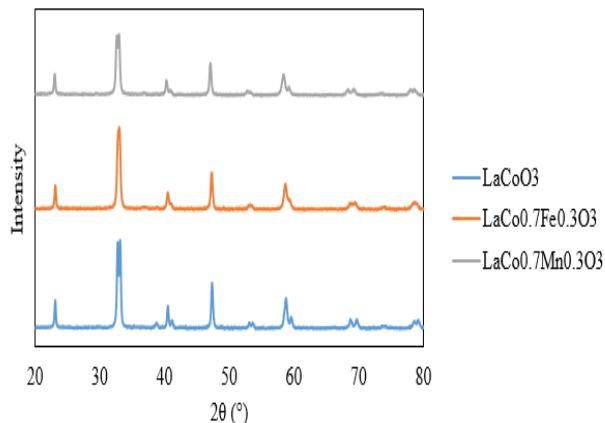

Figure 3. SEM image of $LaBO_3$ (B=Fe, Mn and Co).

Figure 4. Toluene conversion on $LaBO_3$ (B=Fe, Mn and Co).

Table 2

T50 % and T100 % of toluene conversion over $LaBO_3$ (B=Fe, Mn and Co).

Catalyst	T50 %	T100 %
$LaFeO_3$	318	400
$LaMnO_3$	327	----
$LaCoO_3$	276	400

$LaCoO_3$ was modified by substitution of Co by Fe and Mn. $LaCo_{0.7}B'_{0.3}O_3$ (B′=Fe and Mn) perovskites were synthesized by sol-gel method and characterized by XRD. Figure 5 shows XRD patterns of $LaCo_{0.7}B'_{0.3}O_3$. Comparison with standard patterns reveals that XRD pattern of catalysts $LaCoO_3$, $LaFeO_3$ and $LaMnO_3$ confirmed that catalysts have pure perovskite structure. So, it is clear that no second metal oxide phase exists in catalyst structure.

Figure 6 shows toluene conversion for $LaCo_{0.7}B'_{0.3}O_3$ perovskite catalysts. It is chear from Fig. 6, substitution of Co by Fe and Mn increased catalytic activity significantly. $LaCo_{0.7}Mn_{0.3}O_3$ has the highest activity compared to $LaCo_{0.7}Fe_{0.3}O_3$.

Figure 5. XRD patterns of $LaCoO_3$ and $LaCo_{0.7}B'_{0.3}O_3$ (B′=Fe and Mn).

The stability of $LaFeO_3$, $LaMnO_3$ and $LaCoO_3$ was studied at 400 °C for 10 h. The result of the study is shown in Fig. 7. The catalysts showed a strong stability so that after 10 hours, the conversion of toluene reached 93 %, 74 % and 95 % for $LaFeO_3$, $LaMnO_3$ and $LaCoO_3$ respectively.
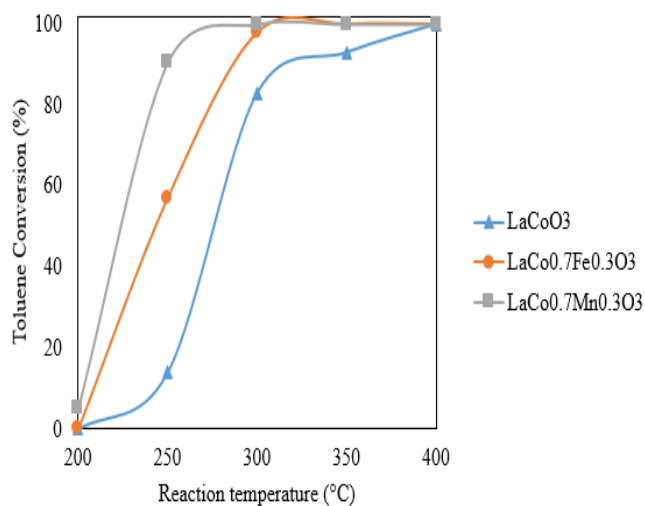

Figure 6. Toluene conversion on $LaCoO_3$ and $LaCo_{0.7}B'_{0.3}O_3$ (B′=Fe and Mn).
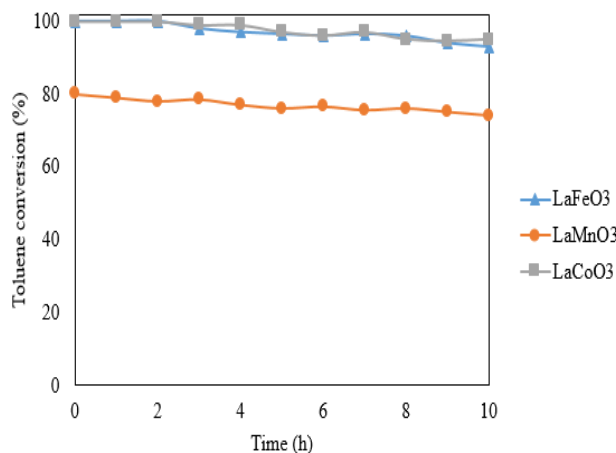
Figure 7. Stability of $LaBO_3$ (B=Fe, Mn and Co) for toluene oxidation.

4. Conclusions

The catalytic activity of $LaBO_3$ (B=Fe, Mn and Co) perovskite catalysts obtained by sol–gel auto combustion method was evaluated in catalytic oxidation of toluene. Perovskite catalysts were characterized by XRD and SEM. XRD results show that single phase perovskite structure was obtained. SEM result shows that size of crystals is close to 100 nm. Based on results, $LaCoO_3$ has the highest activity among $LaBO_3$. For more investigation, $LaCoO_3$ was modified by substitution of Co by other cations. Substitution of Co by Fe and Mn increased the performance of catalysts in toluene oxidation. $LaCo_{0.7}Mn_{0.3}O_3$ is the most active catalyst among the synthesized perovskites.

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