Lanthanum-Based Perovskite-Type Oxides \( \text{La}_{1-x}\text{Ce}_x\text{BO}_3 \) (\( B = \text{Mn and Co} \)) as Catalysts: Synthesis and Characterization

Nyamdavaa Erdenee,1 Uyanga Enkhnaran,1,2 Sevjidsuren Galsan,1 and Altantsog Pagvajav1

1Institute of Physics and Technology, Mongolian Academy of Sciences, 13330 Ulaanbaatar, Mongolia
2Frank Laboratory of Neutron Physics, JINR, Dubna 141980, Russia

Correspondence should be addressed to Nyamdavaa Erdenee; nyam_e@yahoo.com

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\( \text{La}_{1-x}\text{Ce}_x\text{CoO}_3 \) (\( x = 0, 0.2, 0.4 \)) and \( \text{La}_{1-x}\text{Ce}_x\text{MnO}_3 \) (\( x = 0, 0.2 \)) perovskite-type oxides were prepared by sol-gel process. Characterization techniques EDS, FTIR, XRD, BET, and XPS experiments were performed to survey the composition, bulk structure, and the surface properties of perovskites. The reduction behavior, thermal stability, and catalytic activity were studied by \( \text{H}_2 \)-TPR and catalytic performance. All synthesized samples showed well crystalline perovskite structure, 8–22 nm crystallite sizes, and SSA with 2–27 \( \text{m}^2\text{g}^{-1} \). The XRD results showed that the Ce substitution promoted the structural transformation for \( \text{LaCoO}_3 \) from rhombohedral into cubic and for \( \text{LaMnO}_3 \) no change in lattice geometry. Substitution with cerium (\( x = 0.2 \)) showed smaller crystallite size, higher SSA, and the highest reducibility and catalytic activity for \( \text{LaCoO}_3 \).

1. Introduction

Lanthanum-based perovskite-type oxides with general formula \( \text{ABO}_3 \) (\( A = \text{La}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{etc.} ; A = \text{Co}^{3+}, \text{Mn}^{3+}, \text{Sr}^{2+}, \text{etc.} \)) may potentially replace noble metal catalysts due to their high catalytic activity, thermal stability, and low costs [1–3]. On the other hand, these materials present strong limitations for broader application in catalysis such as low surface area resulting from high calcination temperature and oxide instability at high operation temperature [4, 5]. Generally, an increase in the specific surface area of a perovskite-type oxide improves its catalytic activity by increasing the contact area between the catalyst and gas. Particles of perovskite-type oxides, which are the main factor of surface area, are still not small enough, largely because the conventional synthesis processes require calcination at high temperature. Thus, the obtained perovskite particles are heavily agglomerated and sintered, resulting in the low specific surface area [6, 7]. At present, a lot of efforts were carried out for the synthesis of perovskite with improved physical and chemical properties. \( \text{LaBO}_3 \) (\( B = \text{Mn and Co} \)) oxides have been evaluated with materials synthesized through methods such as pechini [8], sol-gel [9], citrate gel [10], and wet impregnation [5] methods.

Among these, the sol-gel method is one of the most effective for the synthesis of nanostructured perovskite-type oxides [11].

It has been reported that the \( \text{ABO}_3 \) perovskites can be properly modified by the partial substitution of atoms at \( A \) or \( B \) which dramatically enhance the activity and significant structural changes, such as lattice distortions, stabilization of multiple oxidation states, or generation of cationic and anionic vacancies. Many studies have reported that partial substitution at the \( A \)-site by a cation of different valence (e.g., \( \text{La}^{3+} \) by \( \text{Ce}^{4+} \) or \( \text{Sr}^{2+} \)) can form oxygen vacancies or change the oxidation state of the \( B \)-site cation, which enhances substantially the catalytic activity [12, 13]. Cerium is usually reported as a good promoter in perovskite lattice. An increase in the cerium substitution level up to 10% on the structure is expected to the enhancement in the activity that explained by oxygen excess in the lattice, cationic vacancies, structural defects, and the presence of multiple \( B \) oxidation states [14].

In this study, nanosized Ce-substituted perovskite-type oxides with \( x \) up to 0.4 were synthesized by sol-gel method and described structural change including Ce distribution. The prepared powder samples were systematically characterized by X-ray diffractometer (XRD), Fourier transform
infrared spectroscopy (FTIR), X-ray absorption spectroscopy (XAS), energy dispersive X-ray spectroscopy (EDS), and Brunauer-Emmett-Teller (BET) surface area analysis, X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction of H\(_2\) (H\(_2\)-TPR). Catalytic activity and selectivity were examined on dehydrogenation propane reaction. Dehydrogenation of propane is attractive in terms of the direct conversion of economic feedstock, which can contribute to the future chemical industry. Perovskite catalysts possess high activities to propylene on this reaction [15].

Our results demonstrated that cerium substituted and nonsubstituted lanthanum-based perovskite-type oxides (La\(_{1−x}\)Ce\(_x\)MnO\(_3\) and La\(_{1−x}\)Ce\(_x\)CoO\(_3\)) show promising structural, surface, electronic states and catalytic properties for catalyst application.

2. Experimental

2.1. Synthesis of the Perovskite. All La\(_{1−x}\)Ce\(_x\)CoO\(_3\) and La\(_{1−x}\)Ce\(_x\)MnO\(_3\) samples were prepared by the sol-gel method, which allows the formation of amorphous citrates of metals with a wide flexibility of compositions [16]. In our preparation procedure, the corresponding nitrates lanthanum (III) nitrate hexahydrate (La(NO\(_3\))\(_3\)·6H\(_2\)O) (Roth, 99.995%), cerium (III) nitrate hexahydrate (Ce(NO\(_3\))\(_3\)·6H\(_2\)O) (Aldrich, 99.95%), and cobalt (II) nitrate monohydrate (Co(NO\(_3\))\(_2\)·H\(_2\)O) (Roth, 99.995%) in the appropriate quantities were dissolved in deionized water to give 0.1M solutions. Citric acid monohydrate was added in 10 wt.% excess over the stoichiometric quantity to insure full complexation of the metal ions. Water was removed on a rotary evaporator at 80°C until the appearance of a gel. The obtained viscous material was dried overnight in a vacuum oven at 100°C. During this treatment, an intense production of nitrogen oxides occurred. The resulting strongly and highly hygroscopic and amorphous material was then crushed and calcined in air for 5 h at 750°C to obtain the desired phases.

2.2. Characterization. XRD data were obtained by using Maxima_X, XRD-7000 equipment with CuK\(_\alpha\) radiation at room temperature. The structural parameters were determined by Rietveld analysis of the diffraction profiles. XAS measurements for Ce L\(_\alpha\), La L\(_\alpha\), and Co K-edges recorded at beam lines BL17C1 of National Synchrotron Center, Hsinchu, Taiwan. The data fitting was performed using the software package IFEFFIT. The specific surface areas were obtained by N\(_2\) adsorption at 77 K, evaluated using the BET equation, on ASAP 2020. EDS elemental analysis was performed using an INCA system. The XPS data was obtained using a VG Scientific ESCALAB MKII spectrometer. The binding energy of the Au (4f\(_{7/2}\)) at 84.0 ± 0.1 eV was used to calibrate the binding energy scale of the spectrometer. XPS spectra smoothening and baseline subtraction were carried out using CasaXPS software. The experiments of the temperature-programmed reduction of H\(_2\) (H\(_2\)-TPR) were carried out on Chem BET TPR/TPD Chemisorption Analyzer from Quantachrome.

<p>| Table I: Weight percentages of the elements present in the samples obtained by EDS analysis. |
|----------------------------------|----------------------------------|----------------------------------|</p>
<table>
<thead>
<tr>
<th>Element</th>
<th>La(_{1−x})Ce(_x)CoO(_3)</th>
<th>La(_{1−x})Ce(_x)MnO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>57.26 ± 0.39</td>
<td>57.50 ± 2.39</td>
</tr>
<tr>
<td>Co/Mn</td>
<td>27.22 ± 6.07</td>
<td>22.95 ± 0.13</td>
</tr>
<tr>
<td>O</td>
<td>15.52 ± 0.39</td>
<td>22.85 ± 1.09</td>
</tr>
<tr>
<td>Ce</td>
<td>9.22 ± 2.37</td>
<td>6.43 ± 1.06</td>
</tr>
</tbody>
</table>

2.3. Catalytic Activity Evaluation. Before the H\(_2\)-TPR experiment, the sample (ca. 0.10 g) was pretreated in an Ar stream at 150°C for 30 min and then cooled to room temperature. After that, a 5% H\(_2\)/Ar mixture stream was switched on and the temperature was increased at a rate of 10°C/min from room temperature to 900°C. The consumption of H\(_2\) in the reactant stream was monitored with a thermal conductivity detector (TCD). The desorbed gases were monitored with a TCD and an online mass spectrometer (MS). The oxidative dehydrogenation of propane reaction was performed at atmospheric pressure in a fixed bed quartz reactor. For each testing, catalyst (ca. 0.20 g) was loaded in a quartz tubular reactor (Φ = 8 mm). The remaining space of the reactor was filled with quartz sand to minimize possible homogeneous reaction [17]. Typical feed gases used were V(C\(_8\)H\(_8\)) = 2 mL min\(^{-1}\), V(O\(_2\)) = 2 mL/min, and V(N\(_2\)) = 16 mL min\(^{-1}\) with a total flow rate of 20 mL min\(^{-1}\). The reaction temperature was changed from 200 to 600°C at 25°C intervals. The highest temperature was consistent with the calcination temperature. The reaction products were analyzed on line by gas chromatography (GC) with a TCD detector using two packed columns, OV-1 column for CH\(_4\), H\(_2\), C\(_2\)H\(_4\), C\(_3\)H\(_6\), and C\(_3\)H\(_8\) separation and TDX-01 column for O\(_2\), CO, CO\(_2\), and CH\(_4\) separation.

3. Results and Discussion

3.1. Elemental Analysis. The elemental compositions of the La\(_{1−x}\)Ce\(_x\)CoO\(_3\) and La\(_{1−x}\)Ce\(_x\)MnO\(_3\) (x = 0, 0.2) perovskites determined by EDS analysis are summarized in Table I. The EDS analysis shows the composition is almost the same (within experimental error) as the nominal composition of the samples.

3.2. FT-IR Spectra. As shown in Figure 1, synthesized La\(_{1−x}\)Ce\(_x\)BO\(_3\) (B = Mn and Co) perovskites had vibration band around 600 cm\(^{-1}\), which could be attributed to the characteristic absorption band of the stretching vibration of Co-O and Mn-O band of BO\(_6\) octahedron. These strong absorption bands are indicating the formation of the perovskite-type structures and found to be shifted towards higher frequency with increases in Ce substitution concentration. Moreover, the intensity of this vibration band increases for x = 0.2 suggesting the change of oxidation state or oxygen vacancies. For the Ce-substituted LaCoO\(_3\) perovskites, a peak observed at 663 cm\(^{-1}\) which can be related to the existence of cobalt cations into Co\(^{2+}\) and Co\(^{3+}\) valence states may be attributed to vibration of Co-O bonds in Co\(_3\)O\(_4\) structure.
The absorption peak at 2361 cm$^{-1}$ and 1644 cm$^{-1}$ is due to the deformation mode of absorbed molecular water of the carrier KBr(H$_2$O)$_n$ and CO$_2$, respectively [18, 19]. The broad band in the region of 3400 cm$^{-1}$ and 1640 cm$^{-1}$ is related to the H-O stretching and H-O-H bending vibration, which are associated with citrates and/or water molecules coordinated with the metal ions.

3.3. Structural Properties. Phase identification of the La$_{1-x}$Ce$_x$CoO$_3$ and La$_{1-x}$Ce$_x$MnO$_3$ (x = 0, 0.2 and 0.4) perovskites, based on the XRD results, is shown in Figure 2. The most important vibration band around 600 cm$^{-1}$ appears sharper for $x = 0.2$ suggesting the perovskite with more symmetrical structure.

The XRD patterns of the La$_{1-x}$Ce$_x$CoO$_3$ (a) and La$_{1-x}$Ce$_x$MnO$_3$ (b) perovskites (x = 0, 0.2, and 0.4) are shown in Figure 2. The most important vibration band around 600 cm$^{-1}$ appears sharper for $x = 0.2$, suggesting the perovskite with more symmetrical structure.

Figure 2: XRD patterns of the La$_{1-x}$Ce$_x$CoO$_3$ (a) and La$_{1-x}$Ce$_x$MnO$_3$ (b) perovskites (x = 0, 0.2, and 0.4). Additional CeO$_2$ phases were revealed for cerium substituted perovskites. The evolution of the CeO$_2$ peaks with increase in substitution is clearly seen.
lattice symmetry. When x is 0.4, characteristic peaks of the Co₃O₄ phase appeared around 37.1° and 56.4°. This conclusion confirms FTIR analysis result. The patterns of LaMnO₃ correspond to the rhombohedral perovskite-type (ICPDS-ICDD 86-1234) and the same lattice geometry observed in Ce-substituted perovskites [21–23]. The substitution x = 0.4, whose peak in the inset is not as sharp as that for the case x = 0.2, and more unreacted CeO₂ aggregates appear.

Therefore, its intensity increases with the addition of cerium due to solubility limit mentioned in the introduction section. The peaks between 32 and 33° indicate that augmentation of Ce concentration leads to broadening and peak shifts in the XRD pattern due to changes or distortions of the cell lattice.

Table 2 summarizes the crystallite size, the BET specific area, and lattice parameters of all samples. The average crystallite size (D) was determined using Debye-Scherrer’s equation $D = \frac{0.9\lambda}{\beta \cos \theta}$, where $\lambda$ is the incident X-ray wavelength ($\lambda_{CuK\alpha} = 1.5443 \, \AA$), $\beta$ is full width at half maximum (FWHM) of the peak corresponding to maximum intensity, and $\theta$ represents the diffraction angle of the most intense peak in degrees. The crystallite size of the samples was found to be in the range of 13 to 8 nm for La₁₋ₓCeₓCoO₃ and relatively larger 22–14 nm for La₁₋ₓCeₓMnO₃ which decreases with Ce content augmentation. That should be expected since the higher Ce⁴⁺ coordination with their surrounding oxygen atoms (within the same crystal plane) than trivalent La³⁺ tends to inhibit crystal growth, resulting in smaller crystal size [24]. Therefore, the crystallite size was increased in La₀.₆Ce₀(2).₄MnO₃ perovskite due to Ce segregation.

3.4. Specific Surface Area. La₁₋ₓCeₓMnO₃ perovskites showed higher specific surface areas (SSA) than La₁₋ₓCeₓCoO₃ which are 19–27 m²/g and 2–5 m²/g, respectively (Table 2). Calcination at high temperature is necessary to obtain the perovskite-type oxides, but such treatment often results in a dramatic decrease in the specific surface area (LaMnO₃ < 30 m²/g and LaCoO₃ < 10 m²/g). Generally, the substituted samples have a larger SSA than pure perovskites and the enhancement was not linear with the substitution. When cerium addition was 0.2, a significant increase in SSA appeared, when x = 0.4, with the increased proportion of additional phases (CeO₂) as shown in XRD profiles and their SSA decreased.

The particle size obtained by XRD and BET can be compared to get the information about agglomeration. If defining $\varphi = \frac{D_{BET}}{D_{XRD}}$ as a factor to reflect the agglomeration extent of the primary crystalline, $\varphi$ value of 1.0 indicates no agglomeration [25]. In this work, agglomeration factors were 2.8, 1.57, and 1.38 for La₁₋ₓCeₓCoO₃ with x = 0, 0.2 and 0.4, respectively. These results suggest that our synthesized perovskites have agglomeration. However, agglomeration factors of La₁₋ₓCeₓCoO₃ show better results compared to La₁₋ₓCeₓMnO₃ perovskites ($\varphi$ = 1.9, 2.15, and 1.53 for x = 0, 0.2, and 0.4, resp.).

3.5. Surface Analysis. The surface compositions of perovskites were studied by XPS. Any charging shift produced in the spectrum by the sample was corrected by taking C ls position (284.6 eV) as a reference line. Table 3 lists the corresponding binding energies of La 3d, O 1s, Ce 3d, Co 2p, and Mn 2p of La₁₋ₓCeₓCoO₃ and La₁₋ₓCeₓMnO₃ perovskite.

### Table 2: XRD and BET analysis results of La₁₋ₓCeₓCoO₃ and La₁₋ₓCeₓMnO₃ (x = 0, 0.2, and 0.4) perovskites. Lattice parameters enlarged due to Ce substitution and the crystallite size decreased with the increase of substitution concentration.

<table>
<thead>
<tr>
<th>Samples</th>
<th>La₁₋ₓCeₓCoO₃</th>
<th>La₁₋ₓCeₓMnO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>x = 0.2</td>
<td>x = 0.4</td>
</tr>
<tr>
<td>$a$ = 5.401, $c$ = 13.312</td>
<td>$a$ = 5.379</td>
<td>$a$ = 5.384</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>12.3</td>
<td>12.8</td>
</tr>
<tr>
<td>SSA (m²/g⁻¹)</td>
<td>2.18</td>
<td>5.68</td>
</tr>
</tbody>
</table>

### Table 3: XPS peak positions and atomic percentages of La₁₋ₓCeₓCoO₃ and La₁₋ₓCeₓMnO₃ perovskites obtained from the fitting of La 3d, Co 3p, Mn 3p, Ce 3d, and O 1s XPS spectra.

<table>
<thead>
<tr>
<th>Samples</th>
<th>LaCoO₃</th>
<th>La₀.₆Ce₀.₄CoO₃</th>
<th>La₀.₄Ce₀.₄CoO₃</th>
<th>La₃CoO₃</th>
<th>La₀.₄Ce₀.₂MnO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>La 3d (eV)</td>
<td>834.3</td>
<td>834.7</td>
<td>834.3</td>
<td>834.7</td>
<td>834.4</td>
</tr>
<tr>
<td>Co 3p/Mn 3p (eV)</td>
<td>779.9</td>
<td>780.2</td>
<td>779.9</td>
<td>641.8</td>
<td>641.8</td>
</tr>
<tr>
<td>O 1s (eV)</td>
<td>528.5</td>
<td>528.8</td>
<td>528.7</td>
<td>528.8</td>
<td>528.9</td>
</tr>
<tr>
<td>Ce⁺⁺⁺ (at. %)</td>
<td>53.1</td>
<td>4.84 (3.9)</td>
<td>53.1</td>
<td>53.1</td>
<td>53.1</td>
</tr>
<tr>
<td>Ce⁺⁺ (at. %)</td>
<td>75.1</td>
<td>73.6</td>
<td>73.4</td>
<td>77.4</td>
<td>74.9</td>
</tr>
<tr>
<td>La (at. %)</td>
<td>15.7</td>
<td>13.2</td>
<td>11.2</td>
<td>17.2</td>
<td>14.2</td>
</tr>
</tbody>
</table>

*The value in parenthesis is a peak percentage (%) of the Ce³⁺ ion.*
Figure 3: La 3d (a), Co and Mn 2p (b), O 1s (c), and Ce 3d (d) core level XPS spectra of La$_{1-x}$Ce$_x$CoO$_3$ and La$_{1-x}$Ce$_x$MnO$_3$ ($x = 0, 0.2,$ and $0.4$) perovskites.

($x = 0, 0.2,$ and $0.4$) samples. The binding energy values of La 3d were recorded around 834 and 851 eV. The other two peaks at 837 and 854 eV are La 3d satellite peaks. These peak positions are similar to the values recorded from pure La$_2$O$_3$ [26], indicating that La ions were in a trivalent state. Moreover, the La 3d$_{5/2}$ and La 3d$_{3/2}$ peaks shifted to higher energy for La$_{0.8}$Ce$_{0.2}$CoO$_3$, which probably connected with different chemical surroundings (Figure 3(a)). Co 2p peaks were occupied at approximately 779.9 eV which indicates Co$^{3+}$ is dominant in of La$_{1-x}$Ce$_x$CoO$_3$ perovskites. When $x = 0.2$, the peak shifted to 780.3 eV that reveals the increasing of Co$^{2+}$ ion content and besides the peak shifted back at $x = 0.4$. According to the XRD results, no Co$_3$O$_4$ phase was observed in $x = 0.2$ perovskite. These findings indicate that Ce$^{3+}$ substitution created Co have lower oxidation states as a charge compensation mechanism. The peaks of Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ are located at 641.8 and 653.1 eV and assigned to Mn$^{3+}$ ions. Moreover, no peak shift was observed for La$_{0.8}$Ce$_{0.2}$MnO$_3$.

Figure 3(c) shows the O 1s core-level spectra of perovskites. The peak at 530.9 eV for the perovskite is due to O$^{2-}$ ions in the lattice and the peak at 532.7 eV can be attributed to adsorbed oxygen such as OH$^-$ whereas adsorbed molecular water was at above 533.2 eV. The adsorbed oxygen decreased at $x = 0.2$ and 0.4 in which proposing cation vacancy defects could be generated as the substitution of Ce ions of perovskites. The ratio of adsorbed and lattice oxygen decreased at $x = 0.2$ of all perovskites which are believed to support reducible oxide structure [27]. XPS spectra of Ce 3d are shown in Figure 3(d). Six different characteristic peaks are indexed to Ce$^{4+}$ and presence of Ce$^{3+}$ ions (inset graph of Figure 3(d)) can also be revealed in perovskites. The Ce$^{4+}$ and Ce$^{3+}$ atomic percentages have been obtained from the area of the peaks by the CasaXPS fitting program (Table 3).

3.6 Temperature-Programmed Reduction. Temperature-programmed reduction profile of La$_{1-x}$Ce$_x$CoO$_3$ and
Table 4: \(\text{H}_2\) consumed for the first step and second step of reduction on \(\text{La}_{1-x}\text{Ce}_x\text{CoO}_3\) and \(\text{La}_{1-x}\text{Ce}_x\text{MnO}_3\) (\(x\) = 0, 0.2, and 0.4) perovskite catalysts.

<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>First step of reduction</th>
<th>Reduction temperature (°C)</th>
<th>Second step of reduction</th>
<th>Reduction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{LaCoO}_3)</td>
<td></td>
<td>391 (surface) 348 (bulk)</td>
<td></td>
<td>648</td>
</tr>
<tr>
<td>(\text{La}_{0.8}\text{Ce}_0.2\text{CoO}_3)</td>
<td>(\text{Co}^{3+}) to (\text{Co}^{2+})</td>
<td>413</td>
<td>(\text{Co}^{2+}) to (\text{Co}^{0})</td>
<td>575</td>
</tr>
<tr>
<td>(\text{La}_{0.8}\text{Ce}_0.2\text{CoO}_3)</td>
<td></td>
<td>427 (surface) 508 (bulk)</td>
<td></td>
<td>616</td>
</tr>
<tr>
<td>(\text{LaMnO}_3)</td>
<td>(\text{Mn}^{3+}) to (\text{Mn}^{2+})</td>
<td>542</td>
<td>(\text{Mn}^{3+}) to (\text{Mn}^{2+})</td>
<td>798</td>
</tr>
<tr>
<td>(\text{La}_{0.8}\text{Ce}_0.2\text{MnO}_3)</td>
<td>(\text{Mn}^{3+}) to (\text{Mn}^{2+})</td>
<td>571</td>
<td>(\text{Mn}^{3+}) to (\text{Mn}^{2+})</td>
<td>798</td>
</tr>
</tbody>
</table>

\(\text{La}_{1-x}\text{Ce}_x\text{MnO}_3\) perovskites are shown in Figure 4. All of the TPR patterns of perovskites including sharp peaks suggest that well-defined crystalline structure is formed. Royer et al. [28] reported two successive steps in TPR profile of \(\text{LaCoO}_3\) perovskite. The first reduction step occurs at low temperature (<500°C) which reduces \(\text{Co}^{3+}\) into \(\text{Co}^{2+}\). The second reduction step (reduction of the \(\text{Co}^{2+}\) into \(\text{Co}^{0}\)) starts at the temperature higher than 600°C. Since \(\text{La}^{2+}\) was nonreducible under the conditions of \(\text{H}_2\)-TPR, the observed \(\text{H}_2\) consumption peaks in the TPR profile of \(\text{LaCoO}_3\) were due to the reduction of \(\text{Co}^{2+}\) cation only.

As seen from \(\text{H}_2\)-TPR profile (Figure 4(a)), the \(\text{H}_2\) consumption provides evidence for the complete reduction of \(\text{Co}^{3+}\) to \(\text{Co}^{0}\) occurring in two steps from \(\text{Co}^{3+}\) to \(\text{Co}^{2+}\) with a peak at about 400°C and \(\text{Co}^{2+}\) to \(\text{Co}^{0}\) centered at about 600°C in agreement with the literature [28]. For \(\text{La}_{1-x}\text{Ce}_x\text{CoO}_3\) perovskite, three reduction peaks were detected which suggest a multiple-step reduction (Table 4). Compared with the pure \(\text{LaCoO}_3\) and \(\text{LaMnO}_3\) perovskites, the two reduction peaks of the Ce-substituted samples all shift to lower temperature direction correspondingly. And \(x = 0.2\) substitution leads to the highest decrease in the reduction peak temperatures and creates an easier reducibility of the \(\text{Co}^{3+}\) into \(\text{Co}^{2+}\). The \(\text{H}_2\)-TPR results supported XPS analysis by showing that cerium substitution increased the reducibility, especially at the temperature range of 300–550°C, suggesting that \(\text{Ce}^{4+}\) increased the number of cation vacancies within the lattice.

Figure 1(b) shows the \(\text{H}_2\)-TPR profile of \(\text{La}_{1-x}\text{Ce}_x\text{MnO}_3\) perovskite catalysts. \(\text{H}_2\) consumption provides evidence for the reduction of \(\text{Mn}^{4+}\) to \(\text{Mn}^{2+}\) occurring in two steps from \(\text{Mn}^{4+}\) to \(\text{Mn}^{3+}\) with a peak maximum at 542°C and reduction of \(\text{Mn}^{3+}\) to \(\text{Mn}^{2+}\) at 798°C. For \(\text{La}_{0.8}\text{Ce}_0.2\text{MnO}_3\) perovskite catalyst, first peak at 571°C and the second peak at 798°C were observed (Table 4). The \(\text{Ce}^{4+}\) insertion decreased the catalyst reducibility of \(\text{Mn}^{4+}\) to \(\text{Mn}^{3+}\) for \(\text{LaMnO}_3\) perovskite, shifting reduction peaks to the higher temperature. But cerium has less influence on the reduction of \(\text{Mn}^{3+}\) to \(\text{Mn}^{2+}\). This indicates that the Mn is reduced to +3 during cerium substitution [29]. Based on the \(\text{H}_2\)-TPR results, it is indicated that the \(\text{La}_{1-x}\text{Ce}_x\text{CoO}_3\) showed higher reducibility (inset of Figure 4) than \(\text{La}_{1-x}\text{Ce}_x\text{MnO}_3\) which was beneficial for catalyst application.

3.7 Catalytic Activity. The values of propane conversion and selectivity as a function of reaction temperature are shown in Figure 5. It can be seen that all Ce-substituted catalysts have better activity than the pure perovskite. Pure \(\text{LaCoO}_3\), as prepared in this work as reference, exhibited very low activity (37.7% conversion and 78.8% selectivity at 500°C). In the case of perovskite samples, ever since the addition of cerium,
the large enhancement of the activity for dehydrogenation of propane was observed and the maximum activity point moved to the lower temperature.

The sample with La$_{1-x}$Ce$_x$CoO$_3$ ($x = 0.2$) gives the best catalytic performance, about 54.6% conversion and 76.8% selectivity at 500°C. When $x$ is 0.4, conversion of 53.7% and selectivity of 75.3% were obtained at the same temperature. At temperatures higher than 500°C, Co$^{n+}$ species coexist with metallic Co$_0$ (supported by H$_2$-TPR experiment) which lead to undesirable methanation reaction [15, 30]. Compared with the perovskite-type oxides, the activity of pure Co$_3$O$_4$ was low, and CeO$_2$ did not even show any activity for dehydrogenation of propane which is not mentioned in these figures. Thus, the additional phases would not contribute much to the catalytic activity directly [13]. Consequently, the La$_{0.8}$Ce$_{0.2}$CoO$_3$ catalyst shows the highest activity and selectivity to propylene on dehydrogenation of propane.

4. Conclusion

In this work, lanthanum-based perovskite-type oxides La$_{1-x}$Ce$_x$BO$_3$ (B = Mn and Co, $x = 0, 0.2$, and 0.4) were successfully synthesized by sol-gel method and investigated as a catalyst. Structural investigations indicated that La$_{1-x}$Ce$_x$MnO$_3$ had a single perovskite structure of rhombohedral and La$_{1-x}$Ce$_x$CoO$_3$ exhibited a transformation in the phase structure (from rhombohedral to the cubic) with increasing cerium content. The estimated optimal average crystallite size is found to be less than 15 nm for both samples. BET results showed an increase (not linear) in the specific surface area upon Ce content. The catalytic activities in the dehydrogenation of propane were enhanced significantly with Ce substitution and achieved the best when $x$ was 0.2 but decreased at 0.4. The cerium substitution when $x = 0.2$ leads to an increase of cation vacancies as charge compensation mechanism and results in enhancement of the catalytic activity, the reducibility, and the selectivity.

Among these catalysts, La$_{0.8}$Ce$_{0.2}$CoO$_3$ catalyst shows best performances with high catalytic activity, selectivity, and stability, suggesting that it may a promising candidate for the catalyst applications. La$_{1-x}$Ce$_x$MnO$_3$ ($x = 0, 0.2$) perovskites with rhombohedral structure show the poorest reducibility as well as the highest specific surface areas. In addition, since we confirmed that the present sol-gel method can be used for perovskite-type oxides with different compositions, it may be useful for SOFC catalyst materials.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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