Deoxygenation of coal bed methane on LaCoO$_3$ perovskite catalyst: the structure evolution and catalytic performance

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A series of perovskite-type LaBO$_3$ (B = Fe, Co, Mn, and Ni) materials have been studied as catalysts for coal bed methane (CBM) deoxygenation. Among them, LaCoO$_3$ shows the best catalytic performance and stability. O$_2$ could be completely eliminated by CH$_4$ to produce CO$_2$ and H$_2$O in the range of 400–720 °C, and the complete deoxidization could be maintained at temperatures of 400, 500, 600, and 660 °C for 100 h. Furthermore, the structure of LaCoO$_3$ could transform from perovskite to Co/La$_2$O$_3$ through La$_2$CoO$_4$/LaCoO$_3$ and La$_2$CoO$_4$/Co$_3$O$_4$ during the process of CBM deoxygenation. The results of H$_2$-TPR and O$_2$-TPO showed the perovskite LaCoO$_3$ is like a smart catalyst, whereby the Co species could reversibly move into and out of the perovskite structure depending on the temperature and reaction atmosphere. When Co species exist in an oxidised state (CoO$_x$, La$_2$CoO$_4$ and/or LaCoO$_3$), the CH$_4$ in CBM is completely oxidized by O$_2$ to produce CO$_2$ and H$_2$O, the results of isotopic tracer experiments and pulse reaction demonstrate that the reaction follows the Mars–van Krevelen mechanism. However, the preferred products of the CBM deoxygenation reaction are CO and H$_2$ on Co/La$_2$O$_3$ through partial oxidation of CH$_4$. With the structure transforming from Co/La$_2$O$_3$ to LaCoO$_3$ after reoxidation by O$_2$, the activity of CBM deoxygenation could be recovered.

1. Introduction

Coal bed methane (CBM), also known as coal mine gas, is a kind of flammable gas whose main component is methane.\(^1\) The direct emission of CBM is not only a waste of energy, but also pollutes the environment, because the warming potential of CH$_4$ is over 20 times of CO$_2$ as a greenhouse gas.\(^2\) At a typical gassy mine, CBM is mainly emitted in three streams: (1) gas drained from the steam before mining, containing 60–95 vol% CH$_4$ and inert gas, which could be directly used or easily used to produce pure CH$_4$; (2) gas drained from the worked areas of the mine, e.g. goaf, containing 30–95 vol% CH$_4$ and some O$_2$ (2–6 vol%); and (3) CH$_4$ ventilation air (0.1–1 vol% CH$_4$).\(^3\)

For the utilization of CBM with high CH$_4$ concentration and low O$_2$ concentration, it is necessary to remove the O$_2$ from the mixture, because the existence of O$_2$ could be dangerous in the process of storage and transportation. Usually, two main methods are used in CBM deoxygenation: non-catalytic and catalytic deoxidization. The common non-catalytic methods include the adsorption of O$_2$, coke burning and deep freezing methods.\(^4,5\) Compared with non-catalytic methods, the catalytic deoxygenation of CBM is a convenient and effective method to eliminate O$_2$ by catalytic combustion of CH$_4$.\(^6,7\) However, the catalytic combustion of CH$_4$ is a violent exothermal reaction with a huge ΔH$_{298}$ of $-802.7$ kJ mol$^{-1}$, which could induce a severe temperature runaway of the reactor and sintering of the catalyst. Meanwhile, the high reaction temperature could cause CH$_4$ partial oxidation and a reforming reaction to produce CO and H$_2$ under the conditions of a large excess of CH$_4$.\(^8,9\)

Therefore, a desirable catalyst used in catalytic deoxygenation of CBM should not only have high activity to remove O$_2$ at low temperatures, but also avoid the production of H$_2$ and CO through side reactions (partial oxidation, cracking and/or reforming reaction) across a wide temperature range.

Furthermore, the composition of the reaction gas in the CBM deoxidization reaction varies from aerobic conditions to reducing conditions with the consumption of O$_2$, which requires the catalyst to maintain high performance under oxidizing and reducing conditions simultaneously. It is another challenge for the deoxygenation catalyst.

Supported noble metal catalysts are widely used in the catalytic combustion of CH$_4$.\(^15,20\) However, the excess CH$_4$ in the reaction gas would lead to particle oxidation or cracking reactions, and produce H$_2$ and CO at temperatures as low as 400 °C while providing high CH$_4$ conversion.\(^21,26\) Lyubovsky et al.\(^27\) prepared Al$_2$O$_3$-supported Pd, Pt and Ru catalysts for CH$_4$
oxidation under both fuel-rich and fuel-lean conditions. The partial oxidation products of H₂ and CO appeared under fuel-rich conditions above the light-off temperature, and their concentration increased with increasing temperature. In addition, the chemical state change of the noble metal in the process of CBM deoxygenation could affect the activity of catalyst. Lu et al.²⁸–³⁰ reported CBM deoxygenation on Pd–PdO–NiO/ Ni-foam and found the oscillation of O₂ conversion to be due to the formation of inert metal Pd under the reducing conditions. The presence of PdNi (alloy) induced by the in situ reaction could eliminate this O₂ oscillation, and O₂ completely oxidized CH₄ to CO₂ and H₂O in the temperature range of 350–500 °C.

Compared with the supported noble metal catalysts, transition metal oxide catalysts (such as Cu, Co Ni etc.) also have attracted great attention.³¹–³³ For example, Tao et al.³⁴ prepared a nano-NiCoO₄ catalyst via a co-precipitation method, which showed high activity for CH₄ combustion under conditions of excess O₂ in the temperature range of 350–550 °C due to the integration of nickel cations, cobalt cations and surface lattice oxygen atoms/oxygen vacancies at the atomic scale.

The perovskite-type oxides (ABO₃) have high temperature stability in hydrocarbon (C₆H₁₂) oxidation³⁵–³⁶ and reforming reactions.³⁷,³⁸ For example, LaCoO₃ and partially substituted LaCoO₃ have been confirmed to have high activities and stabilities for the partial oxidation of CH₄.³⁹–⁴¹ Generally, perovskites prepared with La in the A position, and Co, Mn, Fe or Ni in position B, are used in the catalytic combustion of CH₄.³⁴–⁴⁴ Meanwhile, the temperature of partial oxidation or reforming of CH₄ over perovskite usually exceeds 600 °C, which is much higher than that of supported noble metal catalysts and the transition metal oxide catalysts.⁴⁵–⁴⁷ For example, Slagter and Olsen⁴⁸ studied the partial oxidation of CH₄ to syngas at 800 °C on La–M–O (M = Co, Ni, Rh, and Cr) perovskite catalysts, and found the main product was CO₃ on La–Co–O with the main phase of LaCoO₃, CoO₉, and La₂O₃.

Furthermore, the structure of perovskite-type oxides could be reversibly changed depending on the composition of the reaction atmosphere. Nishihata et al.⁴⁹ reported that LaFe₀.₅₇Co₀.₃₈Pd₀.₅₅O₃ exhibited high catalytic activity during long term ageing, and the Pd reversibly moved into and out of the perovskite lattice during the cycle between oxidative and reductive atmospheres. Hence, the perovskite type catalyst may be a good candidate as a catalyst for CBM deoxygenation, and may be able to remove O₂ from the CBM via CH₄ combustion at a relatively low temperature, and maintain total oxidation across a wide temperature range by prohibiting partial oxidation and other side reactions.

In this work, perovskite-type oxides LaBO₃ (B = Co, Mn, Fe and Ni) were prepared, and the activity and stability of LaBO₃ for CBM catalytic deoxygenation were investigated. The evolution of LaCoO₃ perovskite structure in the reaction and reaction mechanism were also explored.

2. Experimental section

2.1 Catalyst preparation

The perovskite-type oxides (LaBO₃, B = Co, Mn, Fe and Ni) were prepared by the co-precipitation method. A stoichiometric amount of metal nitrate mixture solution and sodium hydroxide solution were simultaneously dropped into a NaOH solution with pH of 9–10 under stirring at 60 °C. The pH value of the mixture solution was kept in the range of 9–10 during the whole precipitation process. The obtained precipitate was aged at 60 °C for 2 h. After being washed by deionized water to neutral pH, the precipitate was filtered and dried at 100 °C for 12 h then calcined in air at 750 °C for 3 h to obtain the LaBO₃ catalysts. The BET surface areas of the prepared LaBO₃ are in the range of 12 to 15 m² g⁻¹.

2.2 Catalyst characterization

The powder X-ray diffraction patterns (XRD) of catalysts were obtained with a Rigaku/D/max 2550 VB/PC diffractometer with a Cu Kα radiation (λ = 1.54056, scanning step 0.02°). Spectra were collected in a range of 2θ = 10–80° with a scanning rate of 6° min⁻¹. In order to obtain more details about the structure of the sample after reduction, the mapping of the elements was measured on the JOEL 2100 instrument operating at 200 kV.

The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an AXIS-Ultra-DLD spectrometer with a Al Kα X-ray source (1486.6 eV). The base pressure inside the analysis chamber was 3 × 10⁻¹⁰ Torr. The XPS spectra of the selected elements were measured with the constant analyzer pass energy of 40 eV. All binding energies (BE) were referenced to the adventitious C 1s peak (BE = 284.8 eV).

The specific surface areas of the catalysts were measured using the N₂ adsorption isotherm at –196 °C by using an automatic Micromeritics ASAP 2020 analyzer.

The temperature-programmed reduction of H₂ (H₂-TPR) experiments were carried out by a conventional flow system equipped with a thermal conductivity detector (TCD). 100 mg catalyst was calcined at 400 °C for 1 h in air before the TPR reaction, and then cooled to room temperature. The pretreated catalyst was heated in a flow of 5 vol% H₂/N₂ (45 mL min⁻¹) at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. After H₂-TPR, the catalyst was maintained at 800 °C for 1 h in a flow of 5 vol% H₂/N₂ (45 mL min⁻¹), then purged with pure He for 1 h. After cooling to room temperature in a He flow, the temperature programmed oxidation of O₂ (O₂-TPO) was performed using the same apparatus; 1 vol% O₂/He (50 mL min⁻¹) was used in O₂-TPO, and the composition of the outlet gas was monitored by an on-line quadrupole mass spectrometer (IPC 400, INFICON Co. Ltd.).

Isotope tracer experiments were conducted in the quartz tube reactor and the effluent gas was monitored by an on-line quadrupole mass spectrometer (MS, IPC 400, INFICON Co. Ltd.).

The catalyst was pretreated at 700 °C for 2.5 h in pure He at 50 mL min⁻¹. 500 mg catalyst was used in the pulse experiments, 517.3 μL of 12 vol% ¹⁸O₂/6 vol% CH₄ was pulsed into the reactor 20 times. 200 mg catalyst was used in the continuous isotope tracer experiments at different designated temperatures, 12 vol% ¹⁸O₂/6 vol% CH₄ was used as the reaction gas.

The reaction orders of O₂ and CH₄ were measured in the temperature range of 340 to 410 °C with feed steams of 4.0–12.0
kPa O₂, CH₄ and N₂. 1.0 kPa CH₄ was used to investigate the catalytic combustion of CH₄, and 50.0 kPa CH₄ was used in the deoxidization of CBM. The O₂/CH₄ conversion was adjusted to below 15% by varying the space velocity in the range of 6000–72 000 mL g⁻¹ h⁻¹ so as to eliminate the thermal effect and diffusion effect.

CH₄ and O₂ pulse experiments were conducted on the same apparatus as that for the isotope tracer experiments. The procedures were as follows: (1) 10 vol% CH₄/He was pulsed into 500 mg catalyst 20 times (CH₄-1st); (2) 20 pulses of pure O₂ was passed through the catalyst bed; (3) step 1 was repeated again (CH₄-2nd). The pulse volume was 517.3 µL.

2.3 Evaluation of the catalytic performance

The catalytic activities of LaBO₃ (B = Co, Mn, Fe and Ni) catalysts for the simulated deoxygenation of CBM were tested in a fixed bed quartz tubular reactor at atmospheric pressure, 300 mg catalyst (40–60 mesh) diluted with 2 g silica sand (20–40 mesh) was used. The feed gas, containing 50 vol% CH₄, 6 vol% O₂ and N₂ to balance, was passed through the catalytic bed at a flow rate of 30 mL min⁻¹. The temperature of the catalyst bed was measured by a thermocouple inserted in the top of the catalyst bed, and the heating rate was 4 °C min⁻¹. An on-line gas chromatograph (Agilent 7890) was used to monitor the composition of the outlet gas. The catalyst activity was expressed by T₁₀ and T₉₀ of O₂, which corresponded to the reaction temperatures required for 10% and 90% O₂ conversion, respectively.

Because the excess CH₄ in the feed gas could lead to partial oxidation or the reforming reaction to produce CO and H₂ at high temperature, the temperature range between the lowest temperature of complete conversion (LTCC) of O₂ and the initial temperature of H₂ formation is defined as the operation window of the catalyst for the deoxygenation reaction.

3. Results

3.1 Catalytic activities of LaBO₃

The catalytic activities of LaBO₃ (B = Co, Fe, Mn and Ni) for CBM deoxygenation are shown in Fig. 1. The type of transition metal in the B-site shows a significant effect on the catalytic activity of the perovskites. LaFeO₃ shows the lowest activity for O₂ elimination, T₁₀ and T₉₀ are 350 and 450 °C, respectively. Meanwhile, LaCoO₃ exhibits the highest catalytic activity, the T₁₀ and T₉₀ are 300 and 390 °C, respectively. Combined with the results of the BET surface area in Table 1, the activity of the catalyst is not directly related to its surface area.

The excess CH₄ in the feed gas could produce H₂ and CO by the partial oxidation or reforming reaction at high reaction temperature (>700 °C). The production of H₂ following the reaction temperature in CBM deoxygenation on different catalysts is shown in Fig. 1b. CO was observed simultaneously but is not shown. The results in Fig. 1b show the initial sequence of H₂ formation is LaFeO₃ < LaMnO₃ < LaNiO₃ < LaCOO₃, and the H₂ formation on LaNiO₃ increases more rapidly than the others when the temperature exceeds 700 °C. Combined with the results in Fig. 1a, LaCoO₃ shows the widest operation window, where O₂ could be completely eliminated by CH₄ in the temperature range of 400 to 720 °C. Continuously increasing the reaction temperature, the amount of H₂ and CO increased rapidly. Therefore, catalyst LaCoO₃ was selected for the further investigation in the following sections.

The stability of LaCoO₃ for deoxygenation reaction was investigated at temperatures of 360, 400, 500, 600, and 660 °C for 100 h. The results in Fig. 2 show O₂ conversion was maintained at 360 °C at about 75% for 100 h, and O₂ could be completely eliminated at 400 and 660 °C for 100 h, and H₂ and CO were not detected during the whole experiments. The same results were obtained at 500 and 600 °C, which are not shown. After reaction at 660 °C for 100 h, the light-off activity of the aged catalyst is nearly consistent with the fresh one (Fig. 2b), which indicates that LaCoO₃ has high stability for the deoxygenation reaction in the temperature range of 400–660 °C.

3.2 XRD

The XRD patterns of the fresh LaBO₃ catalysts are exhibited in Fig. 3. The prepared LaBO₃ (Ni, Mn and Co) show a typical hexagonal perovskite structure. For catalyst LaFeO₃, the major phase is orthorhombic perovskite structure, and some weak diffraction peaks corresponding to Fe₂O₃ and La₂O₃ are also
detected at 2θ = 33, 35, 49 and 54° and 2θ = 26, 30, 39 and 52°, respectively. The cell parameters, crystallite size and BET surface area of the perovskites are listed in Table 1.

Fig. 4 shows the XRD patterns of LaCoO₃ after stability tests at different temperatures. Compared with the results in Fig. 3, there is no observable difference in the LaCoO₃ structure after reaction at 400 and 500 °C for 100 h (Fig. 4a and b), which indicates the stability of the perovskite structure. However, after reaction at 600 °C for 100 h (Fig. 4c), the structure of LaCoO₃ transforms from perovskite into a mixture of perovskite (LaCoO₃, 2θ = 23, 33, 40, 53 and 59°) and perovskite-like (La₃CoO₄, 2θ = 24, 32, 43, 47 and 65°). Continuously increasing the reaction temperature to 660 °C, only perovskite-like La₂CoO₄ and Co₃O₄ crystal phases are detected after 100 h reaction (Fig. 4d). Combined with the results in Fig. 2, it could be concluded that the structure change of LaCoO₃ is dependent on the reaction temperature, but this structure evolution does not bring an apparent difference in the catalytic performance of LaCoO₃ for CBM deoxygenation.

When the deoxygenation reaction is finished at 800 °C, the perovskite structure of LaCoO₃ is completely destroyed, and only La₂O₃ is detected at 26, 30, 39 and 52° (Fig. 4e). The results

Table 1 The cell parameters, crystallite size and BET area of the perovskites

<table>
<thead>
<tr>
<th></th>
<th>LaCoO₃</th>
<th>LaFeO₃</th>
<th>LaMnO₃</th>
<th>LaNiO₃</th>
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</thead>
<tbody>
<tr>
<td>Spatial group</td>
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<td>Orthorhombic</td>
<td>Hexagonal</td>
<td>Hexagonal</td>
</tr>
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<td>a (Å)</td>
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<td>6.0731</td>
<td>5.5953</td>
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<tr>
<td>b (Å)</td>
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<td>6.7968</td>
<td>6.0731</td>
<td>5.5953</td>
</tr>
<tr>
<td>c (Å)</td>
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<td>28.8799</td>
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<td>5.6679</td>
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<tr>
<td>Crystallite size (nm)</td>
<td>39.1</td>
<td>53.72</td>
<td>10.7</td>
<td>26.4</td>
</tr>
<tr>
<td>BET area (m² g⁻¹)</td>
<td>11</td>
<td>16</td>
<td>22</td>
<td>14</td>
</tr>
</tbody>
</table>

a The cell parameters were obtained by Rietveld refinement calculations from the diffractogram of the structures. b The crystallite size was calculated by the Debye–Scherrer formula.

Fig. 2 The stability of LaCoO₃ measured at 360, 400 °C (a) and 660 °C (b). In part (b) the catalytic activity of fresh LaCoO₃ (●) and after reaction at 660 °C for 100 h (○) are compared.

Fig. 4 The XRD patterns of LaCoO₃ after reaction at 400 (a), 500 (b), 600 (c), and 660 °C (d) for 100 h and 800 °C (e), the re-oxidation of sample (e) at 750 °C in air (f) (○: La₂CoO₄; ●: Co₃O₄; ◆: La₂O₃).
in Fig. 1 show the production of $\text{H}_2$ and CO when the reaction temperature was higher than 720 °C, which could lead to the reduction of LaCoO$_3$. The diffraction peaks of Co species cannot be observed, which means Co species are highly dispersed or below the detection limit of XRD. However, it is worth noting that the completely destroyed LaCoO$_3$ could be reverted back to the perovskite structure after reoxidation at 750 °C in air (Fig. 4f).

### 3.3 XPS characterization

XPS characterization is performed to investigate the surface chemical state of the catalysts. Fig. 5 shows the Co 2p spectra of LaCoO$_3$ after reaction at different temperatures (400, 500, 600, and 660 °C) for 100 h. The resolution of the asymmetrical spectra of Co 2p shows the co-existence of two species at BE of 779.8 and 782.1 eV, which could be ascribable to Co$^{3+}$ and Co$^{2+}$, respectively.\(^{50,51}\)

The surface Co$^{2+}$/Co$^{3+}$ ratio of LaCoO$_3$ after reaction is much higher than that of fresh catalyst, and the Co$^{2+}$/Co$^{3+}$ ratio increases with the increase in the reaction temperature as shown in Table 2, which indicates the partial reduction of LaCoO$_3$ during the reaction, and coincides with the results of XRD shown in Fig. 4. The predominant crystal phase changes from perovskite to a mixture of La$_2$CoO$_4$ and Co$_3$O$_4$ through the mixed phase of LaCoO$_3$ and La$_2$CoO$_4$, the average chemical state of the surface Co species is gradually reduced during this process.

### 3.4 Temperature programmed reaction

In order to further investigate the effects of reaction gas and temperature on structure evolution of LaCoO$_3$ during the reaction, experiments of H$_2$-TPR and O$_2$-TPO are carried out.

The H$_2$-TPR profile of fresh LaCoO$_3$ shows three reduction peaks in Fig. 6a. The peaks in the temperature range of 200–500 °C correspond to the reduction of the oxygen adsorbed on the catalyst surface and reduction of Co$^{3+}$ to Co$^{2+}$, the high temperature peak at 500–800 °C could be assigned to the reduction of Co$^{3+}$ to Co$^{2+}$\(^{46,52,53}\). The XRD pattern of Fig. 7a demonstrates that the perovskite structure of LaCoO$_3$ has been completely destroyed and converted to a mixture of metallic Co and La$_2$O$_3$ after H$_2$-TPR, which coincides with that of LaCoO$_3$ after reaction at 800 °C (Fig. 4).

After H$_2$-TPR, O$_2$-TPO of the reduced sample is performed. The result in Fig. 6b shows there are two O$_2$ consumption peaks: a significant peak is located at the range of 200–300 °C and a weak peak is observed at near 700 °C.

For the sample after H$_2$-TPR, XRD results show that the main phases are Co$_3$O$_4$ and La$_2$O$_3$ after reoxidation at 300 °C for 0.5 h (Fig. 7b), which indicates the O$_2$ consumption peak at range of 200–300 °C in Fig. 6b should correspond to the oxidation of metal Co to Co$_3$O$_4$ (Co/La$_2$O$_3$ + O$_2$ → Co$_3$O$_4$ + La$_2$O$_3$). Because the oxidation of metal Co is a strong exothermic reaction, the accumulated heat could result in the direct oxidation of some metallic Co species to Co$^{3+}$. When the oxidation temperature is increased to 750 °C, the perovskite structure of LaCoO$_3$ was recovered (Co$_3$O$_4$ + La$_2$O$_3$ + O$_2$ → LaCoO$_3$), the main phase of

### Table 2

The surface oxygen content (%) and Co$^{2+}$/Co$^{3+}$ ratio of LaCoO$_3$ obtained by XPS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface oxygen content (%)</th>
<th>Co$^{2+}$/Co$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>56.75</td>
<td>0.48</td>
</tr>
<tr>
<td>400 °C</td>
<td>53.72</td>
<td>0.83</td>
</tr>
<tr>
<td>500 °C</td>
<td>49.00</td>
<td>1.26</td>
</tr>
<tr>
<td>600 °C</td>
<td>49.23</td>
<td>3.29</td>
</tr>
<tr>
<td>660 °C</td>
<td>52.68</td>
<td>3.59</td>
</tr>
</tbody>
</table>

*a* After the stability test at specified temperature for 100 h.

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![Fig. 5](image_url)  
**Fig. 5** XPS spectra of fresh LaCoO$_3$ (a) and aged LaCoO$_3$ after stability tests at temperatures of 400 (b), 500 (c), 600 (d) and 660 °C (e) for 100 h.

![Fig. 6](image_url)  
**Fig. 6** H$_2$-TPR (a) and O$_2$-TPO (b) profiles of LaCoO$_3$.  
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the sample is perovskite with a minor Co₃O₄ phase observed at 2θ = 37° (Fig. 7c), which corresponds to the O₂ consumption at the high temperature range in Fig. 6b.

3.5 Kinetic analysis

Fig. 8 shows the pressure-dependent reaction rates on the partial pressure of O₂ (P_O₂) from 4.0 to 12.0 kPa while keeping the partial pressure of CH₄ (P_CH₄) at 1.0 ± 50.0 kPa, which corresponds to the catalytic combustion of CH₄ and deoxygenation of CBM, respectively.

Under O₂ rich conditions, the O₂ reaction rate doesn’t change with an increase in P_O₂, yielding an order of 0 with respect to O₂ at 420 °C. The fact that reaction order of O₂ is about zero shows the O₂ concentration hardly affect the rate of O₂ consumption, which implies the activation of CH₄ is the rate determination step for CH₄ combustion under O₂ excess.

However, under oxygen lean conditions, the O₂ reaction rates increases with an increase in P_O₂, yielding an order of 0.25 with respect to O₂ at 370 °C, which demonstrates that the activation of O₂ is a key factor for CBM deoxygenation reaction. The apparent activation energy (Ea) of deoxygenation reaction on LaCoO₃ is 121 kJ mol⁻¹, as shown in Fig. 9.

3.6 Isotopic tracer experiments

The isotopic tracer pulse reaction results of ¹⁸O₂ + CH₄ are shown in Fig. 10. When the temperature is 600 °C, ¹⁸O₂ (O₂-36) is completely consumed in the 20 pulses on the LaCoO₃ (Fig. 10a), and the production of C¹⁶O₂ (m/z = 44) could be observed at the same time. Furthermore, any CO₂ containing ¹⁸O (m/z = 46 and 48) are not detected, which indicates CH₄ reacts with the lattice oxygen rather than gas ¹⁸O₂. The same results are obtained at the temperature of 700 °C (Fig. 10b).

When the feed gas of 12 vol% ¹⁸O₂/6 vol% CH₄ continuously passes through the catalyst bed at 600 °C, the result in Fig. 11a shows that C¹⁸O₂ is produced immediately and exists as the dominant product in the first 300 s, then the content of C¹⁸O₂ obviously decreases with the increase of reaction time. Meanwhile, the content of C¹⁸O¹⁸O (46) and C¹⁸O₂ (48) increases gradually. After 40 min, C¹⁸O₂ becomes the main product, next is C¹⁶O¹⁸O. Similar results are obtained at 700 °C, as shown in Fig. 11b. Combined with the results in Fig. 10, it may be suggested that the deoxidization reaction of CBM may follow the Mars–van Krevelen mechanism: the CH₄ in the feed gas firstly reacts with lattice oxygen and creates oxygen vacancies, which could be replenished by the diffusion of lattice oxygen from bulk to surface and the adsorption and activation of gas O₂.
3.7 Pulse reaction

The results in Fig. 4 showed structure transformation of LaCoO₃ during the CBM deoxygenation reaction. Separated CH₄ and O₂ pulse reactions on LaCoO₃ and pre-reduced LaCoO₃ at different temperatures are performed to explore the effects of LaCoO₃ structure on the CBM deoxygenation reaction and the formation mechanism of byproducts (H₂ and CO); the results are shown in Fig. 12 and 13.

For the CH₄ pulse reaction on LaCoO₃ at 700 °C (CH₄-1st, Fig. 12a), most of the CH₄ is consumed in 20 pulses, accompanied by the production of CO₂ and H₂O simultaneously. At the same time, weak signals of CO (m/z = 28) are also detected. Based on the standard spectra of CO₂, the CO signals may be induced by dissociative ionisation of CO₂ in the chamber of mass spectrometer. After the CH₄ pulses, 20 pulses of O₂ were passed through catalyst bed, CO₂/CO and H₂O were not detected during this process (not shown).

For the second run of CH₄ pulse reactions (CH₄-2nd, Fig. 12b), the similar results to those in CH₄-1st are obtained, which indicates CH₄ is oxidized by the lattice and/or adsorbed oxygen on LaCoO₃ to produce CO₂ and H₂O, but insufficient lattice oxygen or limited diffusion rate of lattice oxygen from bulk to surface leads to the residual CH₄.

The signals of CO (m/z = 28) in the pulse reaction are induced by the dissociative ionisation of CO₂ in the chamber of mass spectrometer, while not from the reaction production. We have already explained this phenomenon in the CH₄ pulse reaction on LaCoO₃ at 700 °C. However, the results in Fig. 1 show the production of CO and H₂ during the deoxidization reaction when the temperature is higher than 720 °C. It should be noted that the structure of the perovskite LaCoO₃ transforms to Co/La₂O₃ in the deoxidization reaction at a temperature higher than 720 °C (Fig. 4).

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Fig. 10 The pulses test of catalyst LaCoO₃ under the conditions of 12 vol% ¹⁸O₂/6 vol% CH₄ at 600 (a) and 700 °C (b).

Fig. 11 The continuous reaction of 12 vol% ¹⁸O₂/6 vol% CH₄ balanced with N₂ on LaCoO₃ at 600 (a) and 700 °C (b).

Fig. 12 CH₄ pulse reaction at 700 (a, b) and 800 °C (c, d) on LaCoO₃ (a and c are the first run of CH₄ pulse reaction, b and d are the second run).
In order to further investigate CBM deoxygenation reaction on Co/La2O3, the LaCoO3 with perovskite structure is pretreated with 10% H2/N2 at 800 °C to obtain Co/La2O3 (Fig. 7), then the pulse reactions are performed after purging with He for 0.5 h. In the first run of CH4 pulse reaction on Co/La2O3 at 700 °C (Fig. 13a), most of the CH4 is consumed while H2 and CO are not observed during this process, the results are not shown.

During the following O2 pulse reaction, O2 is completely consumed in the 20 pulses due to the oxidation of Co/La2O3. CO/CO2, H2 and H2O are not observed during this process, the results are not shown.

After the O2 pulse reaction, the second run of the CH4 pulse reaction (CH4-2nd) is performed. Fig. 13b shows the production of CO2, CO and H2, and their amount remains nearly constant during the 20 pulses, which is significantly different from the results in Fig. 13a. It may be induced by the partial Co/La2O3 oxidation to CoOx/La2O3 by O2 during the process of the O2 pulse reaction. The formation of CoOx/La2O3 decreases the amount of Co/La2O3, which leads to the significant decrease of CO and H2.

4. Discussion

The results in Fig. 1 and 2 show LaCoO3 behaves with high activity and stability for CBM deoxygenation across a wide temperature range, O2 could be completely eliminated by CH4 to produce CO2 and H2O in the range of 400–720 °C, and the activity of LaCoO3 could be maintained after reaction at 400, 500, 600 or 660 °C for 100 h.

Roseno et al. investigated the structure change of LaCoO3 in partial oxidation of CH4, and found that high temperature reduction could decompose the perovskite structure of LaCoO3 to Co/La2O3, and metallic Co was oxidized to CoO in O2, and further reacted with La2O3 to form La2CoO4 with spinel structure. During CBM deoxidization reaction, the structure of LaCoO3 gradually transfers from perovskite to Co/La2O3 depending on the reaction temperature (Fig. 4). The H2-TPR also showed the structure evolution of LaCoO3 induced by the reduction of H2 in the feed gas. Meanwhile, the destructed perovskite structure could be recovered from Co/La2O3 by calcination or reoxidation (Fig. 4 and 7). The structure evolution of LaCoO3 depending on the temperature and reaction gas is shown schematically in Fig. 14, which demonstrates that Co species could reversibly move into and out of the perovskite structure depending on the temperature and reaction atmosphere.

Based on the results in Fig. 7, the LaCoO3 has been reduced by 5 vol% H2/N2 (45 mL min⁻¹) at 750 °C for 30 min to obtain Co/La2O3 (LaCoO3-R), then Co/La2O3 is reoxidized to perovskite LaCoO3 (LaCoO3-R-O). The activities of CBM deoxygenation in Fig. 15 show that LaCoO3-R behaves with much higher activity than LaCoO3-R-O, and there are no by-products of CO and H2 before 720 °C, as with LaCoO3-R-O. Compared with the result in Fig. 1, LaCoO3-R-O shows nearly the same activity as fresh LaCoO3. Combined with the results in Fig. 6 and 7, the apparently enhanced activity of LaCoO3-R in the low temperature range may be derived from the oxidation of metallic Co by O2. The above results indicate that even if the structure of LaCoO3 with perovskite is completely destroyed when the CBM deoxygenation temperature exceeds 720 °C, the structure and activity could be recovered after calcination at 750 °C in O2. Therefore, LaCoO3 like a smart catalyst, its structure could be reversibly transformed between Co/La2O3, La2CoO4 and LaCoO3 depending on the temperature and reaction atmosphere. This reversible structure evolution of LaCoO3 could meet the challenge of the shift between oxidative and reductive atmosphere typically encountered in CBM deoxygenation.

CH4 combustion over metal oxides catalysts is known to follow a redox mechanism, and a variety of kinetic models for the catalytic combustion of methane, such as the Eley–Rideal, Langmuir–Hinshelwood or Mas–van Krevelen mechanism. The results of isotopic tracer experiments in Fig. 10 and 11 confirms the deoxidization reaction of CBM on LaCoO3 following the Mas–van Krevelen mechanism: the lattice oxygen reacts with CH4 to produce CO2, H2O and oxygen vacancies, and the surface vacancies could be replenished by bulk lattice oxygen and gas O2, which indicates the activation of O2 should be a key factor for CBM deoxygenation reaction. The kinetic data in Fig. 8 also confirmed this. As shown in Fig. 14, LaCoO3 could continuously provide lattice oxygen, accompanying the reduction of perovskite structure to Co/La2O3; meanwhile, O2 gas could be adsorbed and dissociated on the surface, and
incorporated into the lattice of the crystal as $O^{2-}$ species. And therefore, the perovskite LaCoO$_3$ acted as an oxygen pump toward CBM deoxygenization reaction.

The results in Fig. 1 show the O$_2$ could be completely eliminated by CH$_4$ in the temperature range of 400 to 720 °C. As shown in Fig. 14, LaCoO$_3$ could exist as perovskite, La$_2$CoO$_4$/Co$_3$O$_4$ and La$_2$CoO$_4$/LaCoO$_3$ in this temperature range, which indicates that the total oxidation of CH$_4$ by O$_2$ will take place on the catalyst despite the structure transformation of LaCoO$_3$ from perovskite to La$_2$CoO$_4$/Co$_3$O$_4$.

When the reaction temperature exceeds 720 °C, the CO and H$_2$ begin to form and their amounts increase significantly with continuously increasing the temperature (Fig. 1). However, the CO and H$_2$ could not be observed during the CH$_4$ pulse reaction on LaCoO$_3$ even when reaction temperature is 800 °C; the CH$_4$ pulse reaction on reduced LaCoO$_3$ (Co/La$_2$O$_3$) only produces CO and H$_2$ at 700 °C (Fig. 13a). Meanwhile, when Co/La$_2$O$_3$ is partially oxidized to CoO$_2$/La$_2$O$_3$, the co-existence of CoO$_2$/La$_2$O$_3$ and Co/La$_2$O$_3$ results in the formation of CO$_2$ and a significant decrease of CO/H$_2$.

These results show the products of CBM deoxygenation reaction mainly depend on the structure of LaCoO$_3$. When the Co species exists in an oxidised state, such as perovskite, La$_2$CoO$_4$ or CoO$_2$/La$_2$O$_3$, the CBM deoxygenation only produces CO$_2$ and H$_2$O by the total oxidation of CH$_4$. If Co species exists as metal, such as Co/La$_2$O$_3$, the preferred reaction is partial oxidation of CH$_4$, which would lead to the formation of CO and H$_2$.

Therefore, the CBM deoxygenation reaction on LaCoO$_3$ at different temperatures is schematically in Fig. 16. When the reaction temperature is below 720 °C, CH$_4$ reacts with the lattice oxygen to generate CO$_2$ and H$_2$O despite the structure transformation from perovskite to the mixture of Co$_2$O$_4$ and La$_2$CoO$_4$. With further increasing the reaction temperature, the lattice oxygen will be depleted due to the limited amount of O$_2$ in the feed gas and the perovskite structure of LaCoO$_3$ will be completely destroyed. Then, the partial oxidation of CH$_4$ could take place on the surface of metallic Co to produce by-products of CO and H$_2$.

5. Conclusions

The catalyst LaCoO$_3$ prepared by the co-precipitation method exhibits high activity and catalytic stability for the CBM deoxygenation reaction across a wide temperature range. The O$_2$ could be completely eliminated by CH$_4$ to produce CO$_2$ and H$_2$O in the range of 400–720 °C, and complete deoxidization could be maintained in the temperature range of 400–660 °C for 100 h.

The perovskite LaCoO$_3$ acts as a smart catalyst during the process of CMB deoxidization; the structure of LaCoO$_3$ gradually transforms from perovskite to Co/La$_2$O$_3$ through La$_2$CoO$_4$/LaCoO$_3$ and La$_2$CoO$_4$/Co$_3$O$_4$ with the increasing reaction temperature, and these different structures could be transformed into each other depending on the reaction temperature and reaction gas.

When Co species exists as Co$_2$O$_4$, La$_2$CoO$_4$ and/or Co/La$_2$O$_3$, CH$_4$ is completely oxidized by O$_2$ to produce CO$_2$ and H$_2$O. The deoxidization of CBM on catalysts follows the Mars–van Krevelen mechanism, and the activation of O$_2$ was a key factor in the deoxidization of CBM. When Co species exist as metal Co (Co/La$_2$O$_3$), the preferred reaction in CBM deoxygenation would be partial oxidation, which generates CO and H$_2$. However, the complete oxidation of CH$_4$ could be recovered with the structure transformation of Co/La$_2$O$_3$ to LaCoO$_3$ after reoxidation by O$_2$.

Acknowledgements

This project was supported financially by the National Key Research and Development Program of China (2016YFC0204300), the National High Technology Research and Development Program of China (2015AA034603), NSFC of China (21171055, 21333003, 21571061), the “Shu Guang” Project of the Shanghai Municipal Education Commission (12SG29), and the Commission of Science and Technology of Shanghai Municipality (15DZ1205305).
Notes and references
