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Deoxygenation of coal bed methane on LaCoO₃ perovskite catalyst: the structure evolution and catalytic performance

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A series of perovskite-type LaBO₃ (B = Fe, Co, Mn, and Ni) materials have been studied as catalysts for coal bed methane (CBM) deoxygenation. Among them, LaCoO₃ shows the best catalytic performance and stability, O₂ could be completely eliminated by CH₄ to produce CO₂ and H₂O in the range of 400–720 °C, and the complete deoxidation could be maintained at temperatures of 400, 500, 600, and 660 °C for 100 h. Furthermore, the structure of LaCoO₃ could transform from perovskite to Co/La₂O₃ through La₂CoO₄/LaCoO₃ and La₂CoO₄/Co₃O₄ during the process of CBM deoxygenation. The results of H₂-TPR and O₂-TPO showed the perovskite LaCoO₃ 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 (Co₃O₄, La₂CoO₄ and/or LaCoO₃), the CH₄ in CBM is completely oxidized by O₂ to produce CO₂ and H₂O, 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 H₂ on Co/La₂O₃ through partial oxidation of CH₄. With the structure transforming from Co/La₂O₃ to LaCoO₃ after reoxidation by O₂, the activity of CBM deoxygenation could be recovered.

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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 CH₄ is over 20 times of CO₂ 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% CH₄ and inert gas, which could be directly used or easily used to produce pure CH₄; (2) gas drained from the worked areas of the mine, *e.g.* goaf, containing 30–95 vol% CH₄ and some O₂ (2–6 vol%);^{3,4} (3) CH₄ ventilation air (0.1–1 vol% CH₄).⁵

For the utilization of CBM with high CH₄ concentration and low O₂ concentration, it is necessary to remove the O₂ from the mixture, because the existence of O₂ could be dangerous in the process of storage and transportation. Usually, two main methods are used in CBM deoxygenation: non-catalytic and catalytic deoxidation. The common non-catalytic methods include the adsorption of O₂, coke burning and deep freezing

methods.^{6–8} Compared with non-catalytic methods, the catalytic deoxygenation of CBM is a convenient and effective method to eliminate O₂ by catalytic combustion of CH₄.^{9–11} However, the catalytic combustion of CH₄ is a violent exothermal reaction with a huge ΔH_{298} of $-802.7 \text{ kJ mol}^{-1}$, which could induce a severe temperature runaway of the reactor and sintering of the catalyst. Meanwhile, the high reaction temperature could cause CH₄ partial oxidation and a reforming reaction to produce CO and H₂ under the conditions of a large excess of CH₄.^{12–14} Therefore, a desirable catalyst used in catalytic deoxygenation of CBM should not only have high activity to remove O₂ at low temperatures, but also avoid the production of H₂ 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 deoxidation reaction varies from aerobic conditions to reducing conditions with the consumption of O₂, 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 CH₄.^{15–20} However, the excess CH₄ in the reaction gas would lead to particle oxidation or cracking reactions, and produce H₂ and CO at temperatures as low as 400 °C while providing high CH₄ conversion.^{21–26} Lyubovsky *et al.*²⁷ prepared Al₂O₃-supported Pd, Pt and Ru catalysts for CH₄

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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-NiCo₂O₄ 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 (C_nH_{2n+2}) oxidation^{35,36} 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.^{42–45} Meanwhile, the temperature of partial oxidation or reforming of CH₄ over perovskite catalyst usually exceeds 600 °C, which is much higher than that of supported noble metal catalysts and the transition metal oxide catalysts.^{46,47} For example, Slagtern and Olsbye⁴⁸ 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 CO₂ on La–Co–O with the main phase of LaCoO₃, Co₃O₄, 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 LaFe_{0.57}Co_{0.38}Pd_{0.05}O₃ 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 RigakuD/max 2550 VB/PC diffractometer with a Cu K α radiation ($\lambda = 1.54056$, scanning step 0.02°). Spectra were collected in a range of $2\theta = 10$ –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 K α 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 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 μ L 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 deoxygenation 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 *T*₁₀ and *T*₉₀ 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, *T*₁₀ and *T*₉₀ are 350 and 450 °C, respectively. Meanwhile, LaCoO₃ exhibits the highest catalytic activity, the *T*₁₀ and *T*₉₀ 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

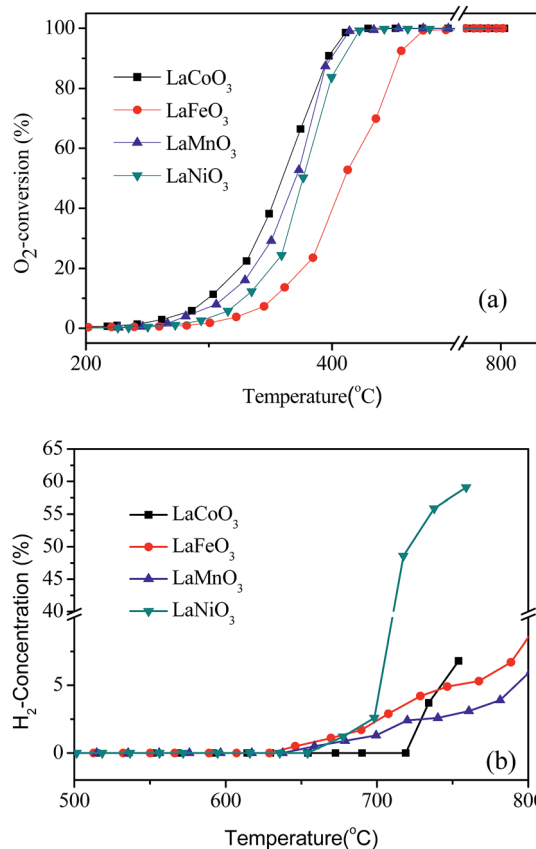


Fig. 1 The conversion of O₂ (a) and production of H₂ (b) in the deoxygenation reaction by LaBO₃ catalysts as a function of temperature.

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



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

	LaCoO ₃	LaFeO ₃	LaMnO ₃	LaNiO ₃
Spatial group	Hexagonal	Orthorhombic	Hexagonal	Hexagonal
<i>a</i> (Å)	5.4358	5.4672	6.0731	5.5953
<i>b</i> (Å)	5.4358	6.7968	6.0731	5.5953
<i>c</i> (Å)	13.0643	28.8799	13.4010	5.6679
Crystallite size (nm)	39.1	53.72	10.7	26.4
BET area (m ² g ⁻¹)	11	16	22	14

^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.

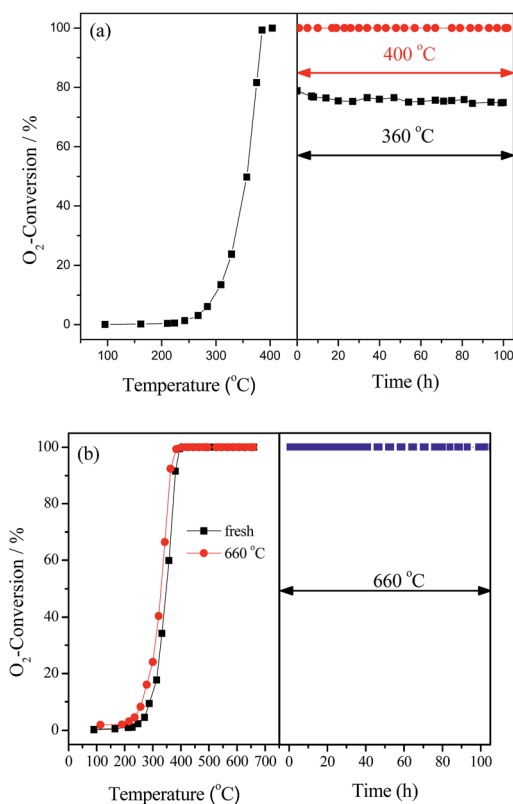


Fig. 2 The stability of LaCoO₃ measured at 360, 400 °C (a) and 660 °C (b). In part (b) the catalytic activity of fresh LaCoO₃ (■) and after reaction at 660 °C for 100 h (●) are compared.

detected at $2\theta = 33, 35, 49$ and 54° and $2\theta = 26, 30, 39$ 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, $2\theta = 23, 33, 40, 53$ and 59°) and perovskite-like (La₂CoO₄, $2\theta = 24, 32, 43, 47$ and 65°). Continuously increasing the reaction temperature to 660 °C, only perovskite-like La₂CoO₄ and Co₃O₄ crystal phases are detected after 100 h

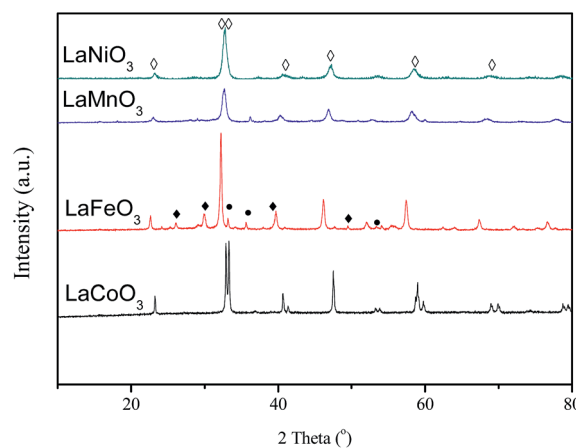


Fig. 3 XRD patterns of LaBO₃ (◇: perovskite; ●: Fe₂O₃; ◆: La₂O₃).

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

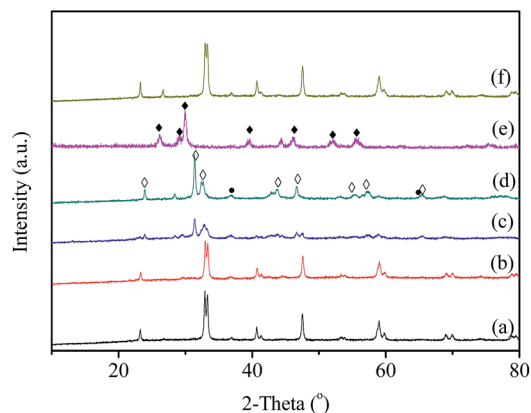


Fig. 4 The XRD patterns of the LaCoO₃ after reaction at 400 (a), 500 (b), 600 (c), and 660 °C (d) for 100 h and 800 °C (e), the re-oxidation of sample (e) at 750 °C in air (f) (◇: La₂CoO₄; ●: Co₃O₄; ◆: La₂O₃).



in Fig. 1 show the production of H₂ and CO when the reaction temperature was higher than 720 °C, which could lead to the reduction of LaCoO₃.⁴⁶ 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 LaCoO₃ 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 LaCoO₃ 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 Co³⁺ and Co²⁺, respectively.^{50,51}

The surface Co²⁺/Co³⁺ ratio of LaCoO₃ after reaction is much higher than that of fresh catalyst, and the Co²⁺/Co³⁺ ratio increases with the increase in the reaction temperature as shown in Table 2, which indicates the partial reduction of LaCoO₃ 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 La₂CoO₄ and Co₃O₄ through the mixed phase of LaCoO₃ and La₂CoO₄, 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 LaCoO₃ during the reaction, experiments of H₂-TPR and O₂-TPO are carried out.

The H₂-TPR profile of fresh LaCoO₃ 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 Co³⁺ to Co²⁺, the high temperature peak at 500–800 °C could be assigned to the reduction of Co²⁺ to Co.^{46,52,53} The XRD pattern of Fig. 7a demonstrates that the perovskite structure of LaCoO₃ has been completely destroyed and converted to a mixture of metallic Co

Table 2 The surface oxygen content (%) and Co²⁺/Co³⁺ ratio of LaCoO₃ obtained by XPS analysis

Sample ^a	Surface oxygen content (%)	Co ²⁺ /Co ³⁺
Fresh	56.75	0.48
400 °C	53.72	0.83
500 °C	49.00	1.26
600 °C	49.23	3.29
660 °C	52.68	3.59

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

and La₂O₃ after H₂-TPR, which coincides with that of LaCoO₃ after reaction at 800 °C (Fig. 4).

After H₂-TPR, O₂-TPO of the reduced sample is performed. The result in Fig. 6b shows there are two O₂ 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 H₂-TPR, XRD results show that the main phases are Co₃O₄ and La₂O₃ after reoxidation at 300 °C for 0.5 h (Fig. 7b), which indicates the O₂ consumption peak at range of 200–300 °C in Fig. 6b should correspond to the oxidation of metal Co to Co₃O₄ (Co/La₂O₃ + O₂ → Co₃O₄ + La₂O₃). 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 Co³⁺. When the oxidation temperature is increased to 750 °C, the perovskite structure of LaCoO₃ was recovered (Co₃O₄ + La₂O₃ + O₂ → LaCoO₃), the main phase of

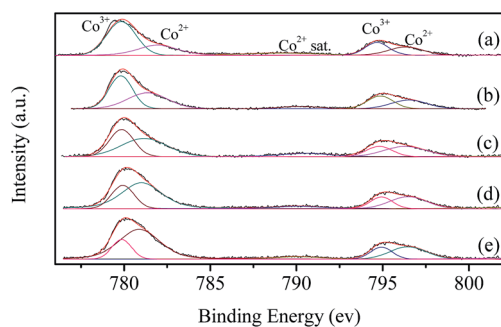


Fig. 5 XPS spectra of fresh LaCoO₃ (a) and aged LaCoO₃ after stability tests at temperatures of 400 (b), 500 (c), 600 (d) and 660 °C (e) for 100 h.

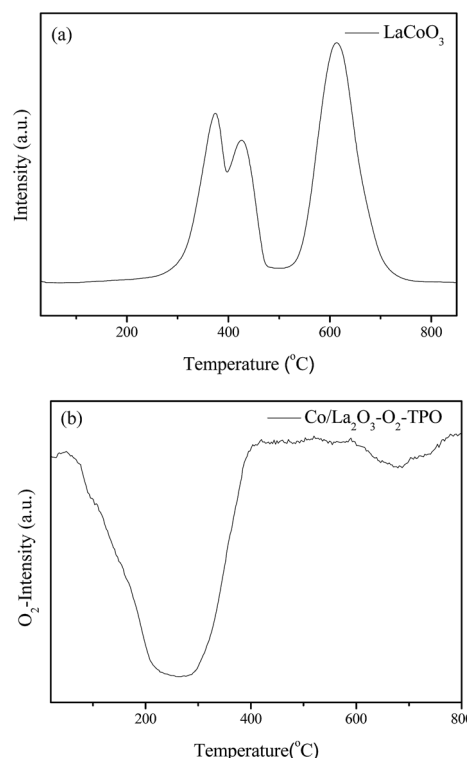


Fig. 6 H₂-TPR (a) and O₂-TPO (b) profiles of LaCoO₃.



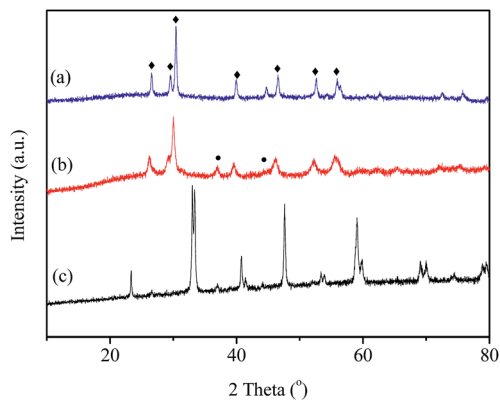


Fig. 7 (a) XRD patterns of LaCoO₃ reduced by H₂ at 800 °C (a); reoxidation by O₂ at 300 °C (b) and 750 °C (c). ●, Co₃O₄; ◆, La₂O₃.

the sample is perovskite with a minor Co₃O₄ phase observed at $2\theta = 37^\circ$ (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_{O_2}) from 4.0 to 12.0 kPa while keeping

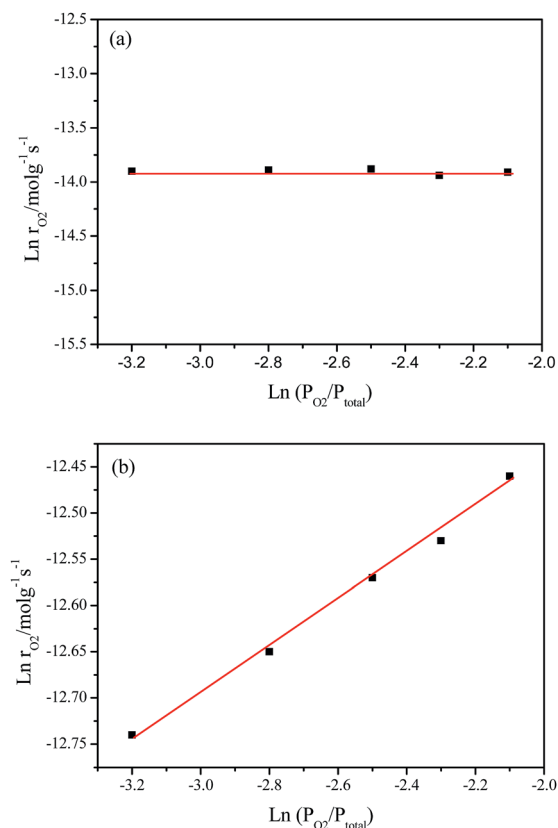


Fig. 8 $\ln r_{O_2}$ as a function of $\ln P_{O_2}$ over LaCoO₃: (a) at 420 °C, the feed gas consisted of 4–12% O₂ and 1% CH₄ at a space velocity of 30 000 mL g⁻¹ h⁻¹; (b) at 370 °C, the feed gas consisted of 4–12% O₂ and 50% CH₄ at a space velocity of 48 000 mL g⁻¹ h⁻¹.

the partial pressure of CH₄ (P_{CH_4}) at 1.0 to 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_{O_2} , 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.^{54,55}

However, under oxygen lean conditions, the O₂ reaction rates increases with an increase in P_{O_2} , 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 (E_a) 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 C¹⁶O₂ is produced immediately and exists as the dominant product in the first 300 s, then the content of C¹⁶O₂ obviously decreases with the increase of reaction time. Meanwhile, the content of C¹⁶O¹⁸O (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 deoxygenation 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.

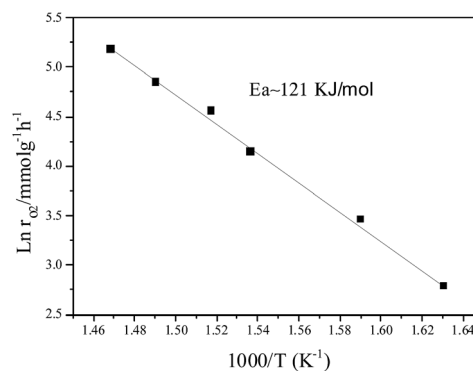


Fig. 9 Arrhenius plot of the reaction rate ($\ln r$) vs. $1/T$ for O₂ deoxygenation over LaCoO₃.



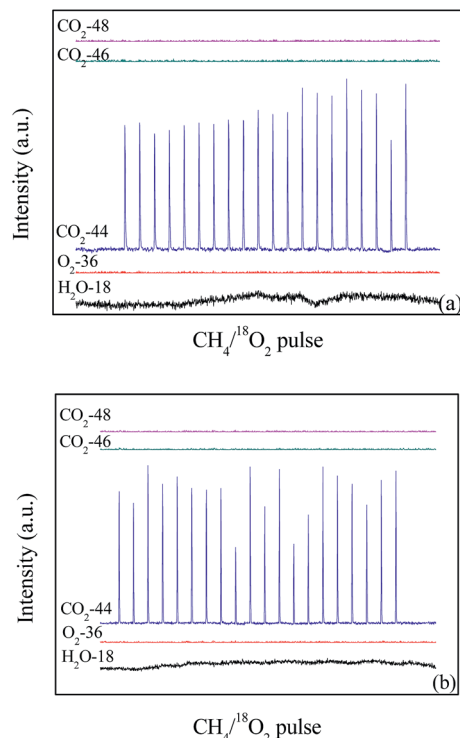


Fig. 10 The pulses test of catalyst LaCoO_3 under the conditions of 12 vol% $^{18}\text{O}_2$ /6 vol% CH_4 at 600 (a) and 700 °C (b).

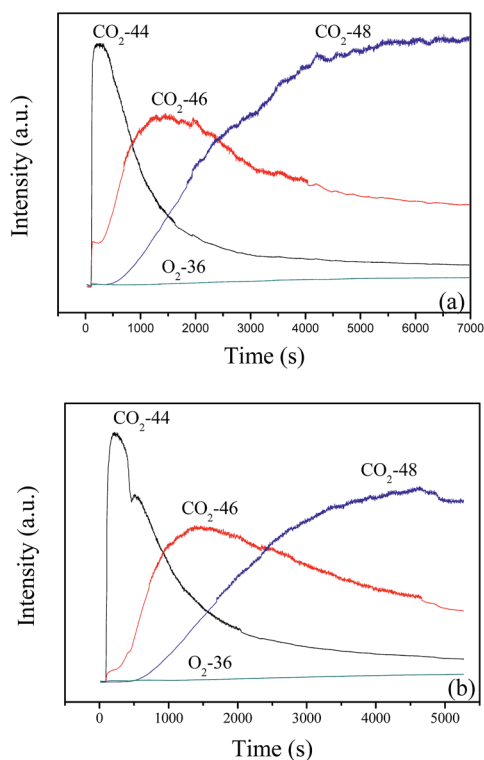


Fig. 11 The continuous reaction of 12 vol% $^{18}\text{O}_2$ /6 vol% CH_4 balanced with N_2 on LaCoO_3 at 600 (a) and 700 °C (b).

3.7 Pulse reaction

The results in Fig. 4 showed structure transformation of LaCoO_3 during the CBM deoxygenation reaction. Separated CH_4 and O_2 pulse reactions on LaCoO_3 and pre-reduced LaCoO_3 at different temperatures are performed to explore the effects of LaCoO_3 structure on the CBM deoxygenation reaction and the formation mechanism of byproducts (H_2 and CO); the results are shown in Fig. 12 and 13.

For the CH_4 pulse reaction on LaCoO_3 at 700 °C (CH_4 -1st, Fig. 12a), most of the CH_4 is consumed in 20 pulses, accompanied by the production of CO_2 and H_2O simultaneously. At the same time, weak signals of CO ($m/z = 28$) are also detected. Based on the standard spectra of CO_2 , the CO signals may be induced by dissociative ionisation of CO_2 in the chamber of mass spectrometer. After the CH_4 pulses, 20 pulses of O_2 were passed through catalyst bed, CO_2/CO and H_2O were not detected during this process (not shown).

For the second run of CH_4 pulse reactions (CH_4 -2nd, Fig. 12b), the similar results to those in CH_4 -1st are obtained, which indicates CH_4 is oxidized by the lattice and/or adsorbed oxygen on LaCoO_3 to produce CO_2 and H_2O , but insufficient lattice oxygen or limited diffusion rate of lattice oxygen from bulk to surface leads to the residual CH_4 .

The signals of CO ($m/z = 28$) in the pulse reaction are induced by the dissociative ionisation of CO_2 in the chamber of mass spectrometer, while not from the reaction production. We have already explained this phenomenon in the CH_4 pulse reaction on LaCoO_3 at 700 °C. However, the results in Fig. 1 show the production of CO and H_2 in the deoxidization reaction when the temperature is higher than 720 °C. It should be noted that the structure of the perovskite LaCoO_3 transforms to $\text{Co}/\text{La}_2\text{O}_3$ in the deoxidization reaction at a temperature higher than 720 °C (Fig. 4).

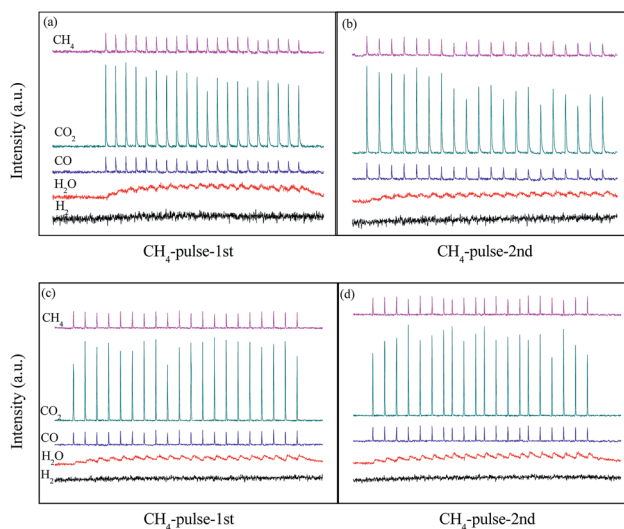


Fig. 12 CH_4 pulse reaction at 700 (a, b) and 800 °C (c, d) on LaCoO_3 (a and c are the first run of CH_4 pulse reaction, b and d are the second run).



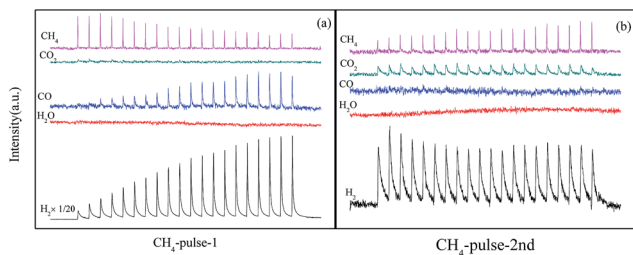


Fig. 13 CH₄ pulse reaction on Co/La₂O₃ at 700 °C (a: first run, b: second run).

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 is generated, and the amount of H₂ and CO significantly increases with an increase in the number of pulses. Meanwhile, a trace amount of CO₂ is detected at the beginning of the pulse reaction, and the amount of CO₂ decreases gradually. After 3 pulses, the CO₂ could hardly be detected.

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 CoO_x/La₂O₃ by O₂ during the process of the O₂ pulse reaction. The formation of CoO_x/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.*³⁹ 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 deoxidation 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.^{49,56,57}

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.^{58,59} The results of isotopic tracer experiments in Fig. 10 and 11 confirms the deoxidation 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

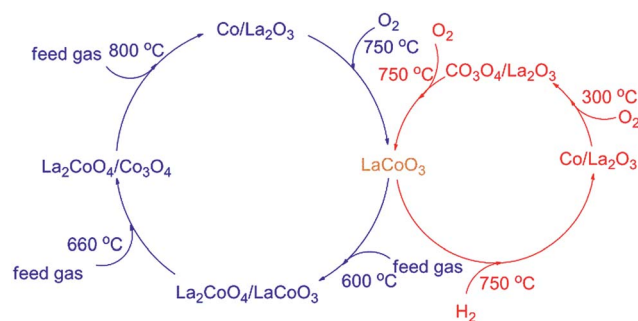


Fig. 14 The structure evolution of LaCoO₃ depending on the reaction gas and temperature.



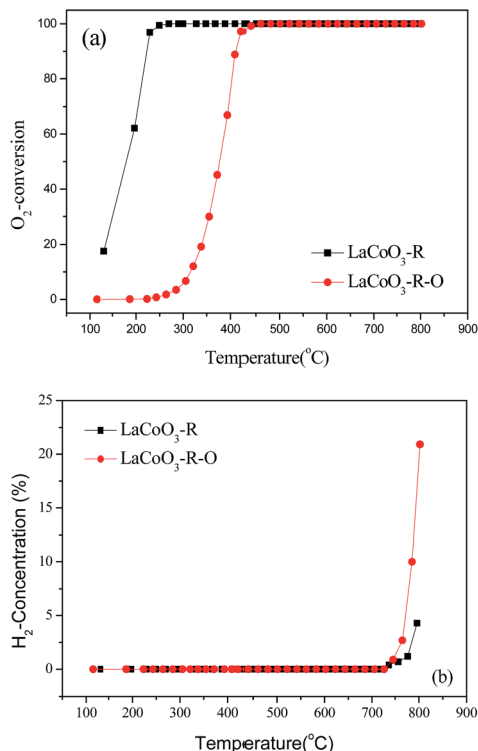


Fig. 15 The conversion of O₂ (a) and production of H₂ (b) over pre-treated LaCoO₃ under different conditions.

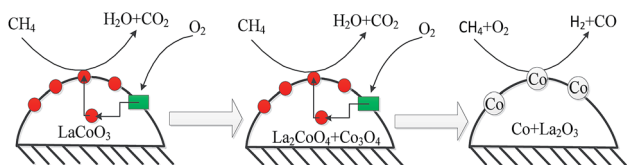


Fig. 16 CBM deoxygenation reaction on the LaCoO₃ catalyst (●: lattice oxygen; ■: oxygen vacancy).

incorporated into the lattice of the crystal as O²⁻ species.^{60,61} And therefore, the perovskite LaCoO₃ acted as an oxygen pump toward CBM deoxidation reaction.⁶²

The results in Fig. 1 show the O₂ could be completely eliminated by CH₄ in the temperature range of 400 to 720 °C. As shown in Fig. 14, LaCoO₃ could exist as perovskite, La₂CoO₄/Co₃O₄ and La₂CoO₄/LaCoO₃ in this temperature range, which indicates that the total oxidation of CH₄ by O₂ will take place on the catalyst despite the structure transformation of LaCoO₃ from perovskite to La₂CoO₄/Co₃O₄.

When the reaction temperature exceeds 720 °C, the CO and H₂ begin to form and their amounts increase significantly with continuously increasing the temperature (Fig. 1). However, the CO and H₂ could not be observed during the CH₄ pulse reaction on LaCoO₃ even when reaction temperature is 800 °C; the CH₄ pulse reaction on reduced LaCoO₃ (Co/La₂O₃) only produces CO and H₂ at 700 °C (Fig. 13a). Meanwhile, when Co/La₂O₃ is partially oxidized to CoO_x/La₂O₃, the co-existence of CoO_x/La₂O₃

and Co/La₂O₃ results in the formation of CO₂ and a significant decrease of CO/H₂.

These results show the products of CBM deoxygenation reaction mainly depend on the structure of LaCoO₃. When the Co species exists in an oxidised state, such as perovskite, La₂CoO₄ or CoO_x/La₂O₃, the CBM deoxygenation only produces CO₂ and H₂O by the total oxidation of CH₄. If Co species exists as metal, such as Co/La₂O₃, the preferred reaction is partial oxidation of CH₄, which would lead to the formation of CO and H₂.

Therefore, the CBM deoxygenation reaction on LaCoO₃ at different temperatures is shown schematically in Fig. 16. When the reaction temperature is below 720 °C, CH₄ reacts with the lattice oxygen to generate CO₂ and H₂O despite the structure transformation from perovskite to the mixture of Co₃O₄ and La₂CoO₄. With further increasing the reaction temperature, the lattice oxygen will be depleted due to the limited amount of O₂ in the feed gas and the perovskite structure of LaCoO₃ will be completely destroyed. Then, the partial oxidation of CH₄ could take place on the surface of metallic Co to produce by-products of CO and H₂.

5. Conclusions

The catalyst LaCoO₃ prepared by the co-precipitation method exhibits high activity and catalytic stability for the CBM deoxidation reaction across a wide temperature range. The O₂ could be completely eliminated by CH₄ to produce CO₂ and H₂O in the range of 400–720 °C, and complete deoxidation could be maintained in the temperature range of 400–660 °C for 100 h.

The perovskite LaCoO₃ acts as a smart catalyst during the process of CMB deoxidation; the structure of LaCoO₃ gradually transforms from perovskite to Co/La₂O₃ through La₂CoO₄/LaCoO₃ and La₂CoO₄/Co₃O₄ 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 Co₃O₄, La₂CoO₄ and/or LaCoO₃, CH₄ is completely oxidized by O₂ to produce CO₂ and H₂O. The deoxidation of CBM on catalysts follows the Mars-van Krevelen mechanism, and the activation of O₂ was a key factor in the deoxidation of CBM. When Co species exist as metal Co (Co/La₂O₃), the preferred reaction in CBM deoxygenation would be partial oxidation, which generates CO and H₂. However, the complete oxidation of CH₄ could be recovered with the structure transformation of Co/La₂O₃ to LaCoO₃ after reoxidation by O₂.

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