

# Tuning surface oxygen species *via* Mg-Ba co-doping on $\text{La}_2\text{O}_3$ to enhance oxidation coupling of methane performance

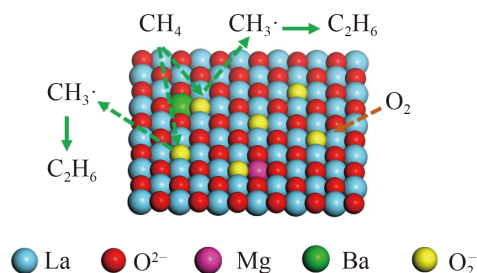
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**Abstract:** Mg-, Ca-, Sr- and Ba-single-doped  $\text{La}_2\text{O}_3$  as well as Mg-Ba co-doped  $\text{La}_2\text{O}_3$  catalysts were synthesized *via* a hydrothermal method and evaluated for the oxidative coupling of methane (OCM). The experimental results revealed that the Mg-modified  $\text{La}_2\text{O}_3$  catalyst activates  $\text{O}_2$  and  $\text{CH}_4$  effectively, yet achieves only moderate  $\text{C}_{2+}$  selectivity. Conversely, the Ba-modified analogue affords high  $\text{C}_{2+}$  selectivity, albeit at the expense of lower reaction activity. Notably, the Mg-Ba co-doped  $\text{La}_2\text{O}_3$  catalyst strikes an effective balance between activity and selectivity, enhancing catalytic performance while maintaining a high  $\text{C}_{2+}$  selectivity. Specifically, at a Mg/Ba molar ratio of 1:1 and 700 °C, it achieved a  $\text{CH}_4$  conversion of 29.5%, a  $\text{C}_{2+}$  selectivity of 54.5% and a corresponding  $\text{C}_{2+}$  yield of 16.1%. The characterization results indicate that Mg and Ba co-doped  $\text{La}_2\text{O}_3$  catalysts promotes the formation of more  $\text{O}_2^-$  species on the catalyst surface, which in turn significantly enhances both the activity and selectivity of  $\text{La}_2\text{O}_3$  catalysts.

**Key words:** oxidation coupling of methane;  $\text{La}_2\text{O}_3$ ; Mg and Ba co-doped;  $\text{O}_2^-$  species



The increasing exploitation of unconventional natural gas resources, such as shale gas and coalbed methane, has investigated the demand for efficient, high-value utilization of methane ( $\text{CH}_4$ )<sup>[1]</sup>. In general,  $\text{CH}_4$  conversion strategies are categorized into indirect and direct pathways. The indirect route typically involves the initial reforming of  $\text{CH}_4$  into synthesis gas (a mixture of CO and  $\text{H}_2$ ), which is then transformed into various high-value chemicals<sup>[2–4]</sup>. However, this multi-step process is often hampered by its complex infrastructure, high energy consumption, and suboptimal carbon atom economy. In contrast, the direct catalytic conversion of  $\text{CH}_4$  into target chemicals offers a more streamlined process with potentially higher efficiency and carbon utilization, presenting a promising frontier in catalysis<sup>[5]</sup>. Within this field, the oxidative coupling of methane (OCM) to  $\text{C}_{2+}$  hydrocarbons ( $\text{C}_{2+}$ ) has garnered

significant research attention due to its conceptual simplicity and potential for direct production of valuable olefins and paraffins in a single step<sup>[6–8]</sup>.

Since the seminal discovery of the OCM reaction in 1982, extensive research has been devoted to developing efficient catalytic systems<sup>[9–11]</sup>. These systems are broadly categorized into four categories: alkali metal/alkaline earth metal oxides (e.g., Li/MgO)<sup>[12]</sup>, multi-component transition metal oxides (e.g.,  $\text{MnO}_x$ - $\text{Na}_2\text{WO}_4/\text{SiO}_2$ )<sup>[13–16]</sup>, composite oxides (e.g.,  $\text{A}_2\text{B}_2\text{O}_7$ )<sup>[17–18]</sup>, and rare earth oxides (e.g.,  $\text{La}_2\text{O}_3$ )<sup>[19]</sup>. While Li/MgO catalysts offer the merits of compositional simplicity and high initial activity, they suffer from the volatility and leaching of lithium species, leading to rapid deactivation<sup>[20–21]</sup>. The benchmark  $\text{MnO}_x$ - $\text{Na}_2\text{WO}_4/\text{SiO}_2$  system delivers exceptional  $\text{C}_{2+}$  selectivity, but this performance typically requires reaction

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temperatures exceeding 800 °C. Under such harsh conditions, the sublimation of the  $\text{Na}_2\text{WO}_4$  active component remains a critical challenge, severely limiting long-term stability<sup>[22–23]</sup>. Composite oxide catalysts exhibit superior structural and thermal robustness, resisting phase transitions at high temperatures. However, they are often hindered by lower  $\text{C}_{2+}$  selectivity due to a higher propensity for the complete oxidation of methane and desired  $\text{C}_2$  products<sup>[24–25]</sup>. In this landscape, rare earth oxides (particularly  $\text{La}_2\text{O}_3$ ) have emerged as promising candidates. They present a balanced profile of high thermal stability and effective catalytic performance under comparatively milder conditions<sup>[26–29]</sup>. Nevertheless, achieving commercially viable  $\text{C}_{2+}$  yields over  $\text{La}_2\text{O}_3$ -based catalysts remains an ongoing research challenge, motivating further efforts in material design and optimization<sup>[30–32]</sup>.

The OCM over  $\text{La}_2\text{O}_3$  primarily involves two key steps: initial activation of  $\text{CH}_4$  on surface active sites to generate methane radicals ( $\text{CH}_3\cdot$ ), followed by their gas-phase coupling to form  $\text{C}_{2+}$  hydrocarbon products. Studies have shown that surface oxygen species (such as  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$  and  $\text{O}^{2-}$ ) play a decisive role in directing activation of  $\text{CH}_4$  to form  $\text{C}_{2+}$  hydrocarbon products or  $\text{CO}_x$ <sup>[32–33]</sup>. Superoxide species ( $\text{O}_2^-$ ) are recognized as crucial for selective C–H bond cleavage, directly abstracting a hydrogen atom from  $\text{CH}_4$  to yield methyl radicals<sup>[34–36]</sup>. This role of  $\text{O}_2^-$  has been corroborated in various catalytic systems, including barium halide-modified  $\text{La}_2\text{O}_3/\text{CaO}$ <sup>[37–38]</sup>,  $\text{La}_2\text{Ce}_2\text{O}_7$ <sup>[35]</sup> and  $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4$  supported on  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ <sup>[34]</sup>. When peroxide species ( $\text{O}_2^{2-}$ ) interact with  $\text{CH}_4$ , one of its oxygen atoms inserts directly into a C–H bond of  $\text{CH}_4$ , forming a methanol intermediate<sup>[39]</sup>. However, under typical OCM reaction temperatures, methanol is very easily overoxidized to  $\text{CO}_2$ , leading to complete oxidation *via* this pathway. Theoretical calculations by Wang et al.<sup>[39]</sup> suggest that the presence of peroxide species ( $\text{O}_2^{2-}$ ) limits the  $\text{C}_{2+}$  selectivity on  $\text{La}_2\text{O}_3$  to only 67%. Although not directly detected experimentally, atomic oxygen anions ( $\text{O}^-$ ) are theorized to form at defect sites on  $\text{La}_2\text{O}_3$ , though their precise role in  $\text{CH}_4$  oxidation remains ambiguous. Lattice oxygen ( $\text{O}^{2-}$ ) species on  $\text{La}_2\text{O}_3$  generally exist in two forms: fully coordinated oxygen bound to lanthanum ions, and coordinatively unsaturated lattice oxygen. The interaction of  $\text{CH}_4$  with surface lattice oxygen ( $\text{O}^{2-}$ ) of the catalyst predominantly leads to the deep oxidation. Therefore, the regulation of oxygen species has become a focus in OCM. Doping  $\text{La}_2\text{O}_3$  with foreign metals is an effective strategy to modulate oxygen species and enhance catalytic performance<sup>[40–41]</sup>. In particular, alkaline earth metal-doped lanthanum-based catalysts can significantly enhance their OCM reaction performance. Kiatsaengthong et al.<sup>[42]</sup> reported that Mg, Ca, Sr and Ba-activated  $\text{La}_2\text{O}_3$  catalysts can boost the  $\text{C}_2$  selectivity by increasing the number of surface superoxide species ( $\text{O}_2^-$ ). Xiong et al.<sup>[43]</sup> studied the effects of Li, Mg, Zn and Ce-doped  $\text{La}_2\text{O}_3$  nanorods on the OCM and found that  $\text{Mg}^{2+}$  doping generates oxygen vacancies, thereby promoting the

formation of more surface oxygen species and enhancing C–C bond coupling.

Co-doping lanthanum oxides with multiple metals has recently emerged as a promising strategy to enhance catalytic performance for the oxidative coupling of methane (OCM) by harnessing synergistic effects between dopants. For instance, Piroli et al.<sup>[44]</sup> demonstrated in Mg- and Ce-modified  $\text{La}_2(\text{Ce}_{1-x}\text{Mg}_x)_2\text{O}_7$  catalysts that Mg incorporation modulates reducibility, stabilizes  $\text{Ce}^{3+}$  species, and creates basic sites, collectively leading to superior  $\text{C}_{2+}$  selectivity at lower temperatures. Sollier et al.<sup>[45]</sup> reported that introducing Sr into  $\text{La}_x\text{Ce}_y\text{O}_z$  solid solutions could promote the formation of structural defects, thereby enhancing the generation of superoxide species ( $\text{O}_2^-$ ). This ultimately achieved a  $\text{C}_{2+}$  yield of 21.7% at 600 °C. Wu et al.<sup>[46]</sup> reported that co-doping of Ca and Sr in  $\text{La}_2\text{Ce}_2\text{O}_7$  could increase surface oxygen vacancies, which elevated the density of surface active oxygen species ( $\text{O}_2^-$ ), resulting in a  $\text{C}_2$  product yield of 21.3% at 650 °C. However, the influence of alkaline-earth metal co-doping on OCM performance over lanthanum-based catalysts, as well as the underlying mechanism regulating the formation of superoxide species ( $\text{O}_2^-$ ), remains inadequately understood.

In this work, a series of  $\text{La}_2\text{O}_3$ -based catalysts modified by single (Mg, Ca, Sr or Ba) and co-doping (Mg and Ba) were prepared by a hydrothermal method. The co-doping strategy, particularly the incorporation of Mg and Ba, was found to significantly enhance both the catalytic activity and  $\text{C}_{2+}$  selectivity for OCM. To gain mechanistic insights into this performance improvement, the structural and chemical properties of the catalysts were interrogated using a combination of characterization techniques. Specifically,  $\text{O}_2/\text{H}_2$ -TPR, *in situ* FT-IR and  $\text{O}_2$  pulse experiments were employed to systematically probe the dynamic activation of  $\text{CH}_4$  and  $\text{O}_2$  as well as the nature and evolution of surface oxygen species on catalysts under relevant conditions. This study clarifies the enhanced oxygen storage and activation behavior and elucidates the synergistic effect of Mg-Ba co-doping in  $\text{La}_2\text{O}_3$ , offering fundamental insights for the rational design of highly active and selective OCM catalysts.

## 1 Experimental

### 1.1 Catalyst preparation

The  $\text{La}_2\text{O}_3$  catalysts co-doped with Mg and Ba were synthesized *via* a hydrothermal-calcination method. Specifically, 18 g of  $\text{NH}_4\text{HCO}_3$  was dissolved in 480 mL of ethylene glycol under vigorous stirring for 60 min. Separately,  $\text{La}(\text{CH}_3\text{COO})_3$ ,  $\text{Ba}(\text{CH}_3\text{COO})_2$  and  $\text{Mg}(\text{CH}_3\text{COO})_2$  (the molar ratio of  $\text{La}(\text{CH}_3\text{COO})_3$ ,  $\text{Ba}(\text{CH}_3\text{COO})_2$  and  $\text{Mg}(\text{CH}_3\text{COO})_2$  was 20:0.5:0.5, with a total amount of 0.04 mol) were dissolved in 480 mL of deionized water. This aqueous solution was then slowly

added dropwise to the  $\text{NH}_4\text{HCO}_3$ /ethylene glycol solution. After stirring at 25 °C for 30 min, the mixture was transferred into a 200 mL Teflon-lined autoclave and maintained at 180 °C for 24 h. The resulting precipitate was collected by centrifugation, washed thoroughly with deionized water and absolute ethanol, and dried at 60 °C overnight. Finally, the dried precursor was calcined in air at 800 °C for 4 h to obtain the catalyst. After cooling to room temperature, the catalyst labeled as  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  was obtained (subscripts represent the molar ratio of elements). In addition, catalysts with alternative La:Mg:Ba ratios of 20:0.2:0.8 and 20:0.8:0.2 were also synthesized, denoted as  $\text{LaMg}_{0.04}\text{Ba}_{0.01}$  and  $\text{LaMg}_{0.01}\text{Ba}_{0.04}$ . A set of single *M*-doped  $\text{La}_2\text{O}_3$  samples (*M* = Mg, Ca, Sr, Ba) were prepared with an *M*:La molar ratio of 0.05:1 and are labeled  $\text{LaM}_{0.05}$ . Pure  $\text{La}_2\text{O}_3$  (La) was obtained using the same procedure with only lanthanum acetate (0.04 mol).

## 1.2 Catalyst characterization

The morphology of the catalysts was characterized by scanning electron microscopy (SEM) on a JSM-7001F scanning electron microscope with a voltage of 5 kV.

The phase of the catalysts was determined by a PANalytical X'pert3 X-ray diffraction analyzer using a Cu target,  $K\alpha$  radiation (wavelength  $\lambda=0.154$  nm), tube current of 50 mA, tube voltage of 50 kV, and a scanning rate of 10(°)/min.

Nitrogen adsorption-desorption isotherms of the catalysts were obtained on a Micromeritics ASAP 2460 physical adsorption analyzer.

XPS testing was performed using an AIX ULTRAADLD X-ray photoelectron spectrometer. The spectra were charge-corrected using the C 1s signal located at 284.5 eV. The O 1s spectra of all samples were fitted using XPSPEAK41 software, and the peaks were resolved using an 80% Gaussian-20% Lorentzian model function. The full width at half maximum (FWHM) of all O 1s spectra was approximately 2 eV.

$\text{O}_2/\text{H}_2$ -TPD testing was conducted using an AMI300 fully automatic chemisorption analyzer. The sample (0.05 g) was first pretreated in a 10%  $\text{H}_2/\text{Ar}$  (volume fraction) at 800 °C for 30 min, then exposed to a 10%  $\text{O}_2/\text{Ar}$  (volume fraction) at 550, 650 or 750 °C for 30 min, subsequently cooled to 50 °C, switched to Ar purging, and finally heated to 850 °C in a 10%  $\text{H}_2/\text{Ar}$  (volume fraction).

*In situ* DRIFT was performed on a Nicolet iS10 infrared spectrometer, collecting 128 scans at a resolution of 4  $\text{cm}^{-1}$ . The sample was pretreated in  $\text{H}_2$  at 680 °C for 10 min, then cooled to 550 °C in Ar. After 10 min, a background

spectrum was collected in Ar. Then, a 5%  $\text{O}_2/\text{Ar}$  (volume fraction) was introduced into the reaction cell, and infrared spectral signals were collected at 550 °C (infrared spectra were labeled as 0, 1, 2, 3, 4, 5 min according to sampling time). Subsequently, the sample was pretreated in  $\text{H}_2$  at 680 °C for 10 min, then cooled to 650 °C in Ar. After running in Ar for 10 min, a background spectrum was collected. A 5%  $\text{O}_2/\text{Ar}$  gas mixture was introduced into the reaction cell, and spectra were collected at 650 °C (infrared spectra were labeled as 0, 1, 2, 3, 4, 5 min according to sampling time).

$\text{O}_2$ -TPD experiments were performed on AutoChem II chemisorption analyzer. The catalyst (0.1 g) was treated with 10%  $\text{O}_2/\text{Ar}$  (volume fraction, 30 mL/min) at 800 °C for 30 min, and cooled to 50 °C in 10%  $\text{O}_2/\text{Ar}$ . At 50 °C, the gas was switched to Ar and purged for 60 min to flatten the baseline. Finally, the temperature was raised to 800 °C under Ar. Results were recorded by a mass spectrometer (MS, IPI GAM200).

$\text{O}_2$  pulse experiments were performed on AutoChem II chemisorption analyzer. The catalyst (0.1 g) was treated with  $\text{H}_2$  (30 mL/min) at 700 °C for 30 min to remove oxygen species, then switched to Ar for 30 min purging. Subsequently, 5%  $\text{CH}_4$  (volume fraction, 30 mL/min) was turned on, and 10 pulses of 5%  $\text{O}_2$  (volume fraction) were performed at 5 min intervals. Results were recorded by a mass spectrometer (MS, IPI GAM200).

## 1.3 Catalyst evaluation

The performance of the catalysts was evaluated in a fixed-bed quartz reactor (inner diameter 8 mm) with a feed gas of  $\text{CH}_4:\text{O}_2=3:1$  ( $\text{CH}_4$  flow rate: 100 mL/min,  $\text{O}_2/\text{N}_2$  flow rate: 66 mL/min) at a space velocity of 80000  $\text{mL}/(\text{g}\cdot\text{h})$ . 0.1 g of catalyst (40–60 mesh) and quartz sand were mixed uniformly to a volume of 0.5 mL and placed in the constant temperature zone of the reactor. Prior to the reaction, the catalyst was pretreated in  $\text{N}_2$  at 800 °C for 2 h, then cooled to 550 °C. Catalytic activity was measured while increasing the temperature from 550 to 800 °C. A chromatograph (Agilent 7890B) equipped with TCD and FID detectors was used for online analysis of feed gas and products.

$\text{CH}_4$  conversion ( $x_{\text{CH}_4}$ ),  $\text{O}_2$  conversion ( $x_{\text{O}_2}$ ),  $\text{C}_{2+}$  selectivity ( $s_{\text{C}_{2+}}$ ), and  $\text{C}_{2+}$  yield ( $Y_{\text{C}_{2+}}$ ) were calculated with the following equations:

$$x_{\text{CH}_4} = \frac{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}}{\text{CH}_{4,\text{in}}} \times 100\% \quad (1)$$

$$x_{\text{O}_2} = \frac{\text{O}_{2,\text{in}} - \text{O}_{2,\text{out}}}{\text{O}_{2,\text{in}}} \times 100\% \quad (2)$$

$$s_{\text{C}_{2+}} = \frac{2 \times (\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6) + 3 \times (\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8) + 4 \times (\text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10})}{2 \times (\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6) + 3 \times (\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8) + 4 \times (\text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10}) + \text{CO} + \text{CO}_2} \times 100\% \quad (3)$$

$$Y_{\text{C}_{2+}} = x_{\text{CH}_4} \times s_{\text{C}_{2+}} \times 100\% \quad (4)$$

## 2 Results and discussion

### 2.1 Reaction performance

Figure 1 presents the OCM reaction performance of Mg, Ca, Sr and Ba doped  $\text{La}_2\text{O}_3$  catalysts within the temperature range of 550–800 °C. The undoped  $\text{La}_2\text{O}_3$  catalyst reaches its optimal performance at 750 °C, with  $\text{CH}_4$  and  $\text{O}_2$  conversions of 30.4% and 95.1%, respectively and a  $\text{C}_{2+}$  selectivity of 48.3%. For alkaline earth metal Mg, Ca, Sr and Ba doped  $\text{La}_2\text{O}_3$  catalysts, a clear trend was observed: the light-off temperature gradually increased with the ionic radius of the dopant. At 600 °C, the order of activity for both  $\text{O}_2$  and  $\text{CH}_4$  conversion was  $\text{LaMg}_{0.05} > \text{LaCa}_{0.05} > \text{LaSr}_{0.05} > \text{LaBa}_{0.05}$ . This sequence indicates that Mg doping significantly enhances the  $\text{O}_2$  activation capability of  $\text{La}_2\text{O}_3$ , leading to improved  $\text{CH}_4$  conversion. Conversely, the  $\text{C}_{2+}$  selectivity showed an opposite trend, increasing with the size of the dopant cation.  $\text{LaBa}_{0.05}$  exhibited the highest  $\text{C}_{2+}$  selectivity, which was 6.7% higher than that of undoped  $\text{La}_2\text{O}_3$  catalyst at 750 °C. However, this gain in selectivity came at the cost of lower activity at 700 °C,  $\text{LaBa}_{0.05}$  showed conversions of only 20.2% for  $\text{CH}_4$  and 59.0% for  $\text{O}_2$ . These results indicate that while Ba doping promotes  $\text{C}_{2+}$  formation, it concurrently weakens the catalyst's oxygen activation capacity, necessitating higher operating temperatures to achieve a competitive  $\text{C}_{2+}$  yield. Motivated by the complementary properties of Mg-doped  $\text{La}_2\text{O}_3$  (strong  $\text{O}_2$  activation) and Ba-doped  $\text{La}_2\text{O}_3$  (high  $\text{C}_{2+}$  selectivity), this study investigates the synergistic integration of both dopants into  $\text{La}_2\text{O}_3$ , aiming to concurrently achieve high  $\text{CH}_4$  conversion and  $\text{C}_{2+}$  selectivity under relatively mild reaction conditions. As

illustrated in Figure 2, the catalytic properties showed a clear dependence on the Mg/Ba molar ratio. Specifically, with an increasing Mg/Ba molar ratio, the  $\text{C}_{2+}$  selectivity progressively increased, while the activation capability for both  $\text{O}_2$  and  $\text{CH}_4$  concurrently decreased. The catalyst with an equimolar Mg/Ba ratio ( $\text{LaMg}_{0.025}\text{Ba}_{0.025}$ ) demonstrated balanced and superior performance at 700 °C, achieving a  $\text{CH}_4$  conversion of 29.5% and a  $\text{C}_{2+}$  selectivity of 54.5%. This represents a 6% enhancement in  $\text{C}_{2+}$  selectivity compared to the solely Mg-doped counterpart ( $\text{LaMg}_{0.05}$ ) and an 11% improvement in  $\text{CH}_4$  conversion relative to the solely Ba-doped catalyst ( $\text{LaBa}_{0.05}$ ) at the same temperature. Therefore, the synergistic co-doping of Mg and Ba into  $\text{La}_2\text{O}_3$  successfully reconciled the trade-off between activity and selectivity at 700 °C, yielding a substantially higher  $\text{C}_{2+}$  yield. In addition, the long-term stability of the optimal  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst was evaluated under industrially relevant, high-severity conditions ( $\text{GHSV} = 80000 \text{ mL}/(\text{g} \cdot \text{h})$ ). As shown in Figure 3(a), the catalyst maintained exceptionally stable  $\text{CH}_4$  conversion and  $\text{C}_{2+}$  selectivity over the 24 h test, showing its robustness, which is crucial for the OCM reaction.

The composition distribution of  $\text{C}_{2+}$  products over the  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst was analyzed as a function of temperature (Figure 3(b)). Below 700 °C, the products were mainly  $\text{C}_2$  hydrocarbons ( $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ ), with no  $\text{C}_{3+}$  products detected. As the temperature increased, longer-chain  $\text{C}_{3+}$  products began to form, and their selectivity gradually increased. The ratio of  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  in  $\text{C}_2$  hydrocarbon products (Figure 3(c), (d)) continued to increase with temperature, indicating that higher temperatures promote the dehydrogenation of  $\text{C}_2\text{H}_6$ , thereby favoring the formation of the higher-value product,  $\text{C}_2\text{H}_4$ .

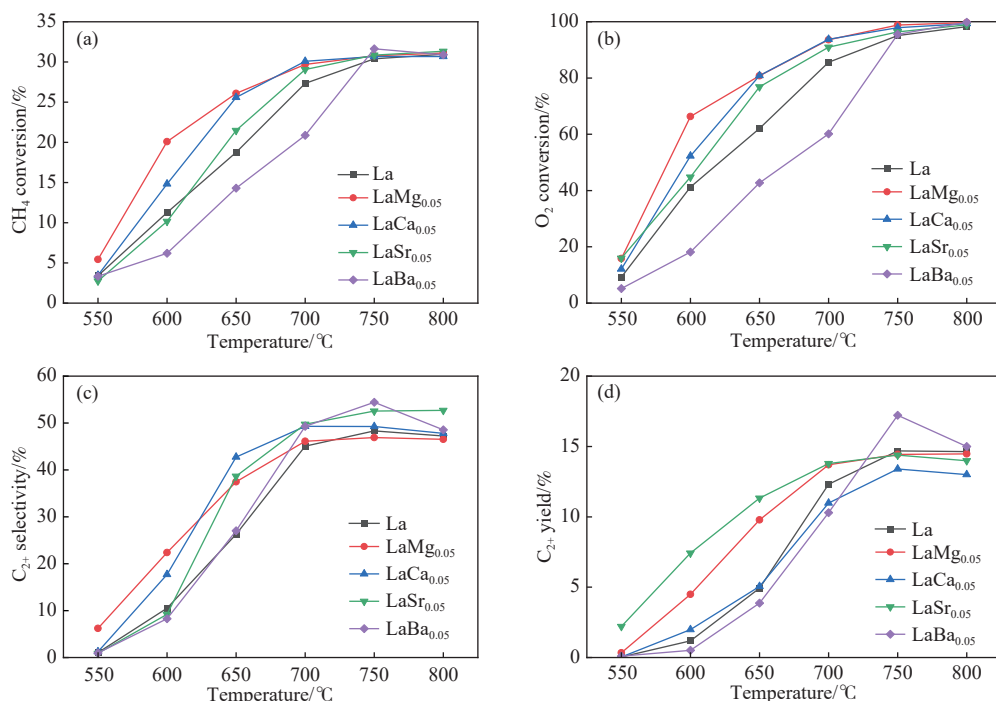


Fig. 1 (a)  $\text{CH}_4$  conversion, (b)  $\text{O}_2$  conversion, (c)  $\text{C}_{2+}$  hydrocarbon selectivity, (d)  $\text{C}_{2+}$  hydrocarbon yield of pure phase  $\text{La}_2\text{O}_3$  and Mg, Ca, Sr, Ba single-doped  $\text{La}_2\text{O}_3$  catalysts

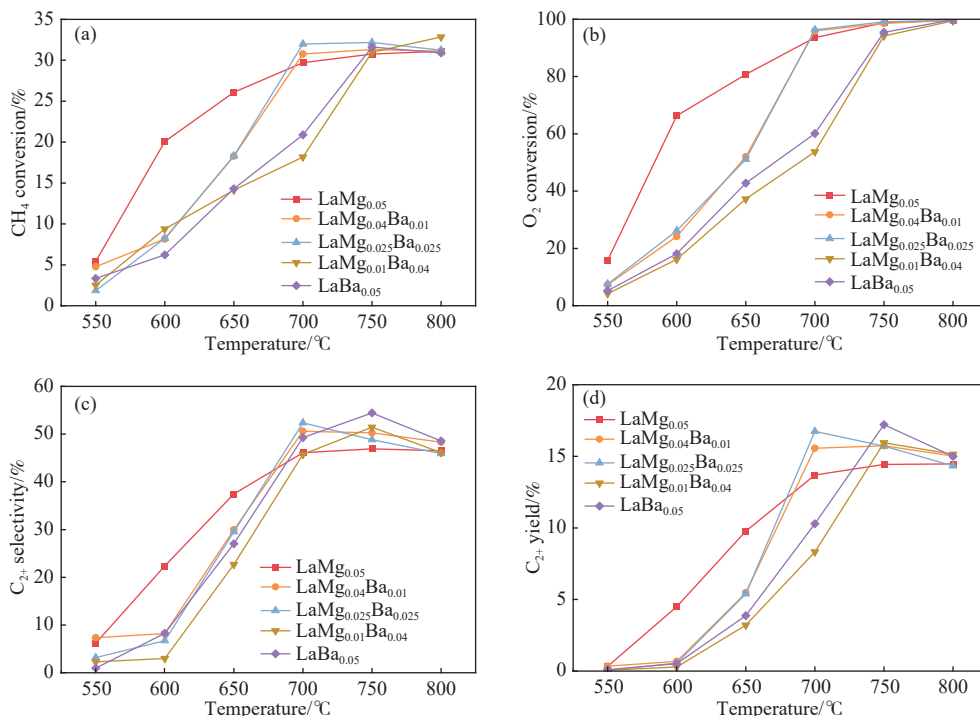


Fig. 2 (a)  $\text{CH}_4$  conversion, (b)  $\text{O}_2$  conversion, (c)  $\text{C}_{2+}$  hydrocarbon selectivity, (d)  $\text{C}_{2+}$  hydrocarbon yield of Mg and Ba single-doped  $\text{La}_2\text{O}_3$  and different Mg and Ba ratio co-doped  $\text{La}_2\text{O}_3$  catalysts

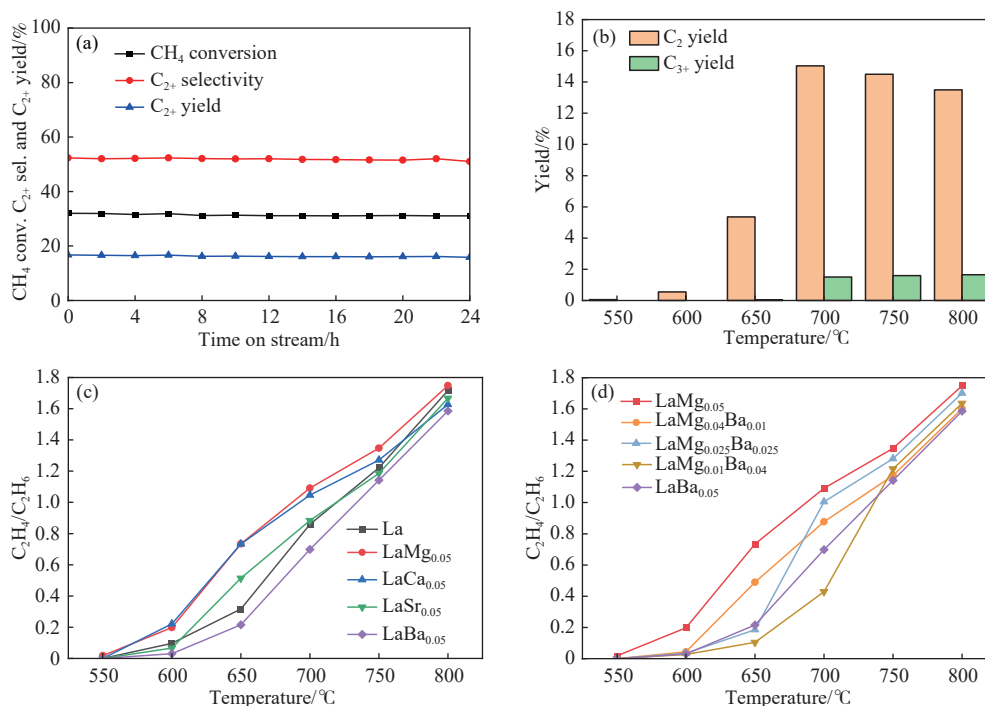


Fig. 3 (a) stability test of  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst at 700 °C, (b) the  $\text{C}_{2+}$  composition distribution of  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst, (c) and (d) the  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  of catalysts

## 2.2 Catalyst structure

Figure 4 shows the XRD patterns of alkaline earth metal doped  $\text{La}_2\text{O}_3$  catalysts. All diffraction patterns for both single-doped (Mg, Ca, Sr, Ba) and co-doped (Mg-Ba) catalysts correspond exclusively to the hexagonal phase of

$\text{La}_2\text{O}_3$  (PDF#05-0602)<sup>[43]</sup>. No diffraction peaks corresponding to oxides or carbonates of the doped elements were observed, indicating high dispersion of the alkaline-earth metals within the  $\text{La}_2\text{O}_3$ . A comparison of the XRD patterns revealed that the diffraction peak of  $\text{La}_2\text{O}_3$  (101) crystal plane corresponding to Mg and Ca single-

doped  $\text{La}_2\text{O}_3$  catalysts shifted toward higher angles. This shift results from the smaller ionic radii of  $\text{Mg}^{2+}$  (0.072 nm) and  $\text{Ca}^{2+}$  (0.100 nm) compared with  $\text{La}^{3+}$  (0.103 nm), which induce lattice contraction and a reduction in the interplanar spacing. In contrast, the (101) peak shifts to lower angles for the Sr- and Ba-doped samples due to the larger ionic radii of  $\text{Sr}^{2+}$  (0.118 nm) and  $\text{Ba}^{2+}$  (0.135 nm), leading to lattice expansion. The above analysis confirms that the successful incorporation of the dopant ions into the  $\text{La}_2\text{O}_3$  lattice. Furthermore, the magnitude of the shift increased with the atomic radius of the dopant. A similar trend was observed in the co-doped samples, with  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  exhibiting the most pronounced shift toward lower angles, suggesting the formation of a greater number of structural defects.

Figure 5 shows SEM images of La,  $\text{LaMg}_{0.05}$ ,  $\text{LaBa}_{0.05}$ ,  $\text{LaMg}_{0.04}\text{Ba}_{0.01}$ ,  $\text{LaMg}_{0.01}\text{Ba}_{0.04}$  and  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalysts. The undoped  $\text{La}_2\text{O}_3$  catalyst exhibited a well-defined triangular flake morphology. Upon doping with alkaline earth metals, all modified catalysts  $\text{LaMg}_{0.05}$ ,  $\text{LaBa}_{0.05}$ ,  $\text{LaMg}_{0.04}\text{Ba}_{0.01}$ ,  $\text{LaMg}_{0.01}\text{Ba}_{0.04}$  and  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  retained the characteristic triangular lamellar morphology, indicating that alkaline earth metal doping treatment does not affect the fundamental morphology of the catalysts. However, the doped catalyst exhibited a more open, loosely packed lamellar structure with a developed microporous texture, which is expected to facilitate reactant diffusion and enhance mass transport during the reaction.

The specific surface area and pore volume of the catalysts were determined, and the results are shown in Table 1. Compared to pure  $\text{La}_2\text{O}_3$ , the alkaline-earth-metal-doped

catalysts showed increased specific surface area and pore volume. A larger specific surface area can expose more surface active sites<sup>[46]</sup>, which is beneficial for catalytic reactions.

### 2.3 Characterization of surface oxygen species

The reducibility of adsorbed oxygen species on Mg- and Ba-doped  $\text{La}_2\text{O}_3$  catalysts was analyzed by  $\text{O}_2/\text{H}_2$ -TPR. All catalysts were first reduced in  $\text{H}_2$  to remove oxygen species adsorbed, followed by exposure to  $\text{O}_2$  at different temperatures (550, 650 and 750 °C) to (re)adsorb oxygen. Afterward,  $\text{H}_2$  temperature-programmed reduction was performed, and the amount of reducible oxygen species was quantified based on the  $\text{H}_2$  consumption peaks. The characterization results are shown in Figure 6. All catalysts showed three distinct  $\text{H}_2$  consumption peaks, corresponding to the reduction of different oxygen species: a low-temperature  $\text{H}_2$  consumption peak (200–300 °C) assigned to the reduction of oxygen species adsorbed on the catalyst surface; a medium-temperature  $\text{H}_2$  consumption peak (300–500 °C) attributed to the reduction of oxygen species oxygen migrating from the near-surface region; and a high-temperature  $\text{H}_2$  consumption peak above 500 °C associated with the reduction of bulk-phase oxygen species diffusing to the surface. With increasing  $\text{O}_2$  pretreatment temperature, the areas of the low- and medium-temperature  $\text{H}_2$  consumption peaks gradually increased, indicating that the number of reducible oxygen species on its surface and near-surface layer increased with  $\text{O}_2$  pretreatment temperature.

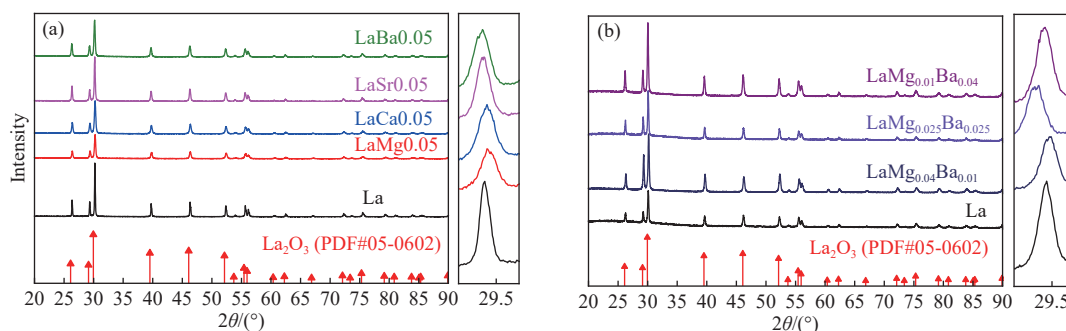


Fig. 4 XRD patterns of (a)  $\text{La}_2\text{O}_3$  in pure phase and  $\text{La}_2\text{O}_3$  mono-doped with Mg, Ca, Sr and Ba, (b)  $\text{La}_2\text{O}_3$  catalysts co-doped with different ratios of Mg and Ba

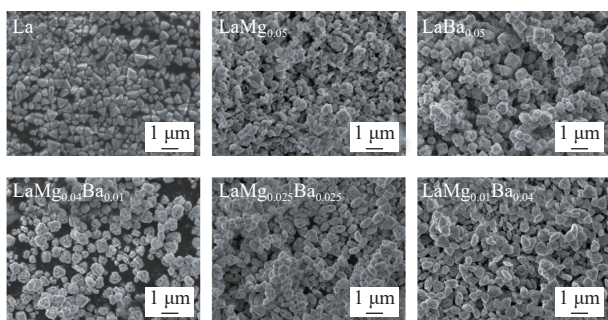
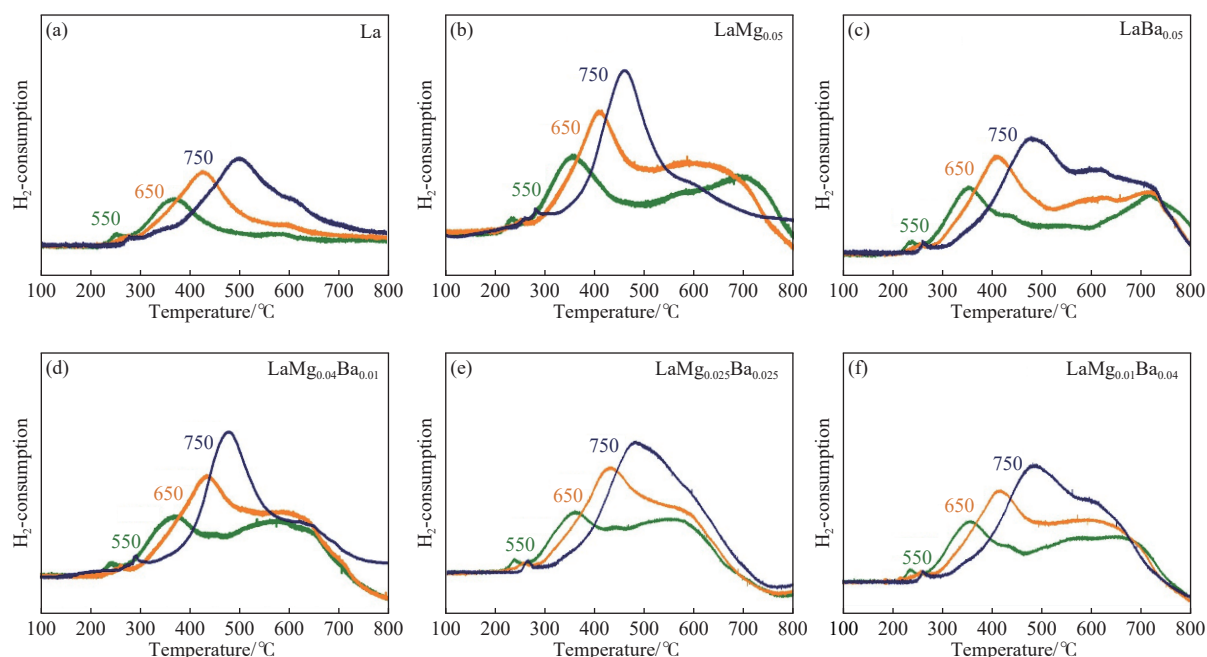


Fig. 5 SEM images of Mg and Ba modified  $\text{La}_2\text{O}_3$  catalysts

Table 1 Weave properties of alkaline earth metal-doped

| Sample                                 | $\text{La}_2\text{O}_3$ catalysts                          |                                                              |
|----------------------------------------|------------------------------------------------------------|--------------------------------------------------------------|
|                                        | BET surface area<br>$S^a/(\text{m}^2 \cdot \text{g}^{-1})$ | Total pore volume<br>$V^b/(\text{cm}^3 \cdot \text{g}^{-1})$ |
| La                                     | 3                                                          | 0.02                                                         |
| $\text{LaMg}_{0.05}$                   | 12                                                         | 0.06                                                         |
| $\text{LaBa}_{0.05}$                   | 11                                                         | 0.04                                                         |
| $\text{LaMg}_{0.04}\text{Ba}_{0.01}$   | 13                                                         | 0.05                                                         |
| $\text{LaMg}_{0.025}\text{Ba}_{0.025}$ | 10                                                         | 0.04                                                         |
| $\text{LaMg}_{0.01}\text{Ba}_{0.04}$   | 13                                                         | 0.06                                                         |

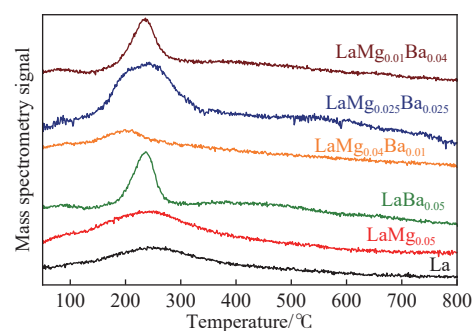
<sup>a</sup>: Calculated with the BET equation; <sup>b</sup>: Referring to the BJH desorption pore volume.

Fig. 6 O<sub>2</sub>/H<sub>2</sub>-TPR profiles of Mg and Ba modified La<sub>2</sub>O<sub>3</sub> catalysts

This trend indicates an enhanced ability of catalysts to adsorb and activate O<sub>2</sub> at elevated temperatures. Moreover, this trend correlates well with the observed increase in O<sub>2</sub> conversion with temperature, suggesting that the abundance of active oxygen species is a key factor governing O<sub>2</sub> conversion, which in turn drives CH<sub>4</sub> conversion. Furthermore, as the O<sub>2</sub> treatment temperature increased, the high-temperature H<sub>2</sub> consumption peak of the LaMg<sub>0.05</sub> catalyst moved toward lower temperatures, suggesting that bulk phase oxygen migrated to the sub-surface layer and merged with near-surface oxygen species, which reflects its strong capacity for O<sub>2</sub> dissociation and explains its highest O<sub>2</sub> conversion at 600 °C. In contrast, the LaBa<sub>0.05</sub> catalyst had a relatively weak ability to dissociate O<sub>2</sub>, thus resulting in the lowest O<sub>2</sub> conversion at 600 °C. The relatively weak O<sub>2</sub> dissociation capacity of the LaBa<sub>0.05</sub> catalyst may be associated with enhanced C<sub>2+</sub> selectivity, as dissociated oxygen species frequently lead to the complete oxidation of CH<sub>4</sub><sup>[44]</sup>. In Mg and Ba co-doped La<sub>2</sub>O<sub>3</sub> catalysts, as the O<sub>2</sub> pretreatment temperature increased, the phenomenon of oxygen species in the bulk phase migrating to the sub-surface layer was also observed. Especially under the O<sub>2</sub> pretreatment condition of 750 °C, the high-temperature H<sub>2</sub> consumption peaks of LaMg<sub>0.04</sub>Ba<sub>0.01</sub> and LaMg<sub>0.025</sub>Ba<sub>0.025</sub> catalysts merged with the medium-temperature H<sub>2</sub> consumption peaks. This feature indicates that LaMg<sub>0.04</sub>Ba<sub>0.01</sub> and LaMg<sub>0.025</sub>Ba<sub>0.025</sub> catalysts possess excellent capabilities in activating O<sub>2</sub> and generating active oxygen species, thus enabling high O<sub>2</sub> conversion and CH<sub>4</sub> conversion at a reaction temperature of 700 °C.

The effects of single-doping (with Mg or Ba) and co-doping (with Mg and Ba) modifications on the surface oxygen species of La<sub>2</sub>O<sub>3</sub> catalysts were investigated by O<sub>2</sub>-TPD, as shown in Figure 7. All catalysts displayed distinct O<sub>2</sub> desorption peaks in the range of 200–300 °C, which are

ascribed to chemisorbed oxygen species, such as superoxide (O<sub>2</sub><sup>-</sup>) and peroxide (O<sub>2</sub><sup>2-</sup>) ions<sup>[18,38,46]</sup>. Comparing the O<sub>2</sub> desorption profiles of Mg and Ba single-doped and co-doped La<sub>2</sub>O<sub>3</sub> catalysts, the O<sub>2</sub> desorption peak of Mg-modified La<sub>2</sub>O<sub>3</sub> was broad, suggesting the presence of multiple types of chemisorbed oxygen species on its surface. The Ba-modified sample presented a sharp desorption peak, indicating the formation of a more uniform type of chemisorbed oxygen species on its surface. When Mg and Ba were co-doped at a 1:1 molar ratio (LaMg<sub>0.025</sub>Ba<sub>0.025</sub>), the desorption peak became broader and its intensity increased. Correlating with catalyst performance, the Mg and Ba co-doped LaMg<sub>0.025</sub>Ba<sub>0.025</sub> catalyst achieved 96.3% O<sub>2</sub> conversion at 700 °C, whereas LaMg<sub>0.05</sub> and LaBa<sub>0.05</sub> required 750 °C to exceed 95% O<sub>2</sub> conversion. This indicates that the Mg and Ba co-doping enhanced the activation capacity for O<sub>2</sub>, significantly increasing both the type and quantity of surface chemisorbed oxygen species. It should be noted that the desorption peaks in this temperature regime may encompass both superoxide (O<sub>2</sub><sup>-</sup>) and peroxide (O<sub>2</sub><sup>2-</sup>) species, whose similar thermal stabilities make their precise deconvolution challenging<sup>[47]</sup>.

Fig. 7 O<sub>2</sub>-TPD profiles of Mg and Ba modified La<sub>2</sub>O<sub>3</sub> catalysts

The surface oxygen species distributions of  $\text{La}_2\text{O}_3$  catalysts, modified by single (Mg or Ba) and co-doping (Mg-Ba), were analyzed via XPS, with results presented in Figure 8 and Table 2. The O 1s spectra can be deconvoluted into three characteristic peaks, corresponding to  $\text{O}_2^-$  (532 eV),  $\text{CO}_3^{2-}$  (531 eV), and  $\text{O}^{2-}$  (529 eV) respectively<sup>[18,26,35]</sup>. Moreover, the quantitative results of surface oxygen species indicate that the concentration of  $\text{O}_2^-$  is significantly enhanced in Mg and Ba co-doped  $\text{La}_2\text{O}_3$  catalysts, with the  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst exhibiting the highest  $\text{O}_2^-$  concentration. However, XPS analysis cannot reflect the true surface state of the catalyst under high-temperature reaction conditions. Moreover, La-based catalysts easily adsorb  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to generate carbonates and hydroxyl groups, which seriously interfere with the O 1s signal and compromise the accuracy of active-oxygen quantification. Therefore, to investigate reactive oxygen species under reaction conditions, *in situ* DRIFT experiments were conducted.

*In situ* DRIFT was employed to further investigate the types of surface active oxygen species on La-based catalysts, and the results are shown in Figure 9. Both Mg and Ba single-doped and co-doped  $\text{La}_2\text{O}_3$  catalysts exhibit an infrared band at approximately  $1100\text{ cm}^{-1}$ , which is assigned to surface superoxide species ( $\text{O}_2^-$ )<sup>[43]</sup>. In contrast,

undoped  $\text{La}_2\text{O}_3$  exhibits no detectable signal for surface superoxide species ( $\text{O}_2^-$ ). As the temperature of the  $\text{O}_2$  treatment increased, the intensity of the band at  $1100\text{ cm}^{-1}$  enhanced, indicating that the amount of superoxide species ( $\text{O}_2^-$ ) generated on the catalyst increased with rising temperature. This trend correlates with the temperature-dependent increase in  $\text{C}_{2+}$  selectivity observed for these catalysts, further confirming that superoxide species ( $\text{O}_2^-$ ) serve as the active oxygen species in the reaction. Specifically, for the  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst, both the intensity of the  $\text{O}_2^-$  signal and the  $\text{C}_{2+}$  selectivity increased with temperature, with the latter rising from 3% to 52%. Doping with either Mg or Ba effectively promotes the formation of superoxide species ( $\text{O}_2^-$ ) on the  $\text{La}_2\text{O}_3$  surface. Notably, the signal for superoxide species ( $\text{O}_2^-$ ) of  $\text{LaBa}_{0.05}$  was significantly stronger than that of  $\text{LaMg}_{0.05}$ . This may be attributed to the strong charge-induced dipole interaction between Ba with a larger ionic radius and superoxide species ( $\text{O}_2^-$ ), which can stabilize superoxide species ( $\text{O}_2^-$ )<sup>[48]</sup>. Importantly, compared to single-doped catalysts, the signal for superoxide species ( $\text{O}_2^-$ ) was markedly enhanced in Mg and Ba co-doped  $\text{La}_2\text{O}_3$  catalyst, demonstrating a synergistic effect of Mg and Ba in promoting the formation of superoxide species ( $\text{O}_2^-$ ).

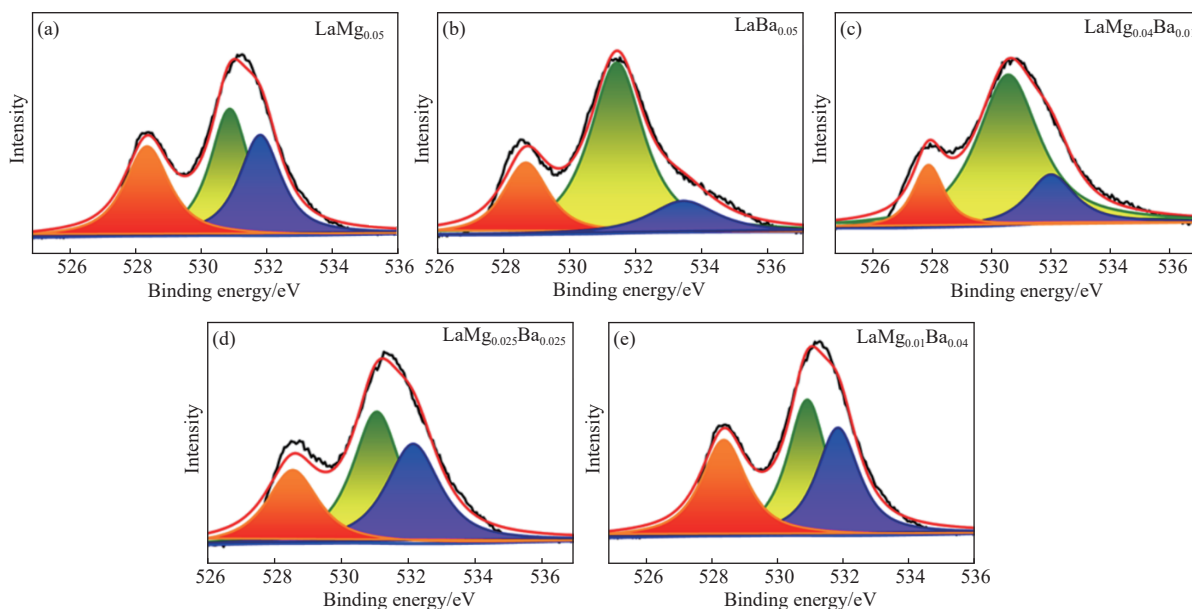


Fig. 8 XPS O 1s spectra of Mg and Ba modified  $\text{La}_2\text{O}_3$  catalysts

Table 2 Curve-fitting and quantification results of XPS O 1s spectra

| Catalyst                               | O 1s binding energy/eV (percentage fraction/%) |                    |                 | $\text{O}_2^-/\text{O}^{2-}$ |
|----------------------------------------|------------------------------------------------|--------------------|-----------------|------------------------------|
|                                        | $\text{O}_2^-$                                 | $\text{CO}_3^{2-}$ | $\text{O}^{2-}$ |                              |
| $\text{LaMg}_{0.05}$                   | 532.2 (13.4)                                   | 531.6 (68.2)       | 528.9 (18.3)    | 0.7                          |
| $\text{LaBa}_{0.05}$                   | 533.2 (14.2)                                   | 531.4 (63.2)       | 528.7 (22.6)    | 0.6                          |
| $\text{LaMg}_{0.04}\text{Ba}_{0.01}$   | 532.1 (16.7)                                   | 530.7 (68.8)       | 528.1 (14.3)    | 1.2                          |
| $\text{LaMg}_{0.025}\text{Ba}_{0.025}$ | 532.2 (34.6)                                   | 531.1 (41.1)       | 528.6 (24.1)    | 1.4                          |
| $\text{LaMg}_{0.01}\text{Ba}_{0.04}$   | 532.2 (31.8)                                   | 530.9 (37.6)       | 528.5 (30.4)    | 1.0                          |

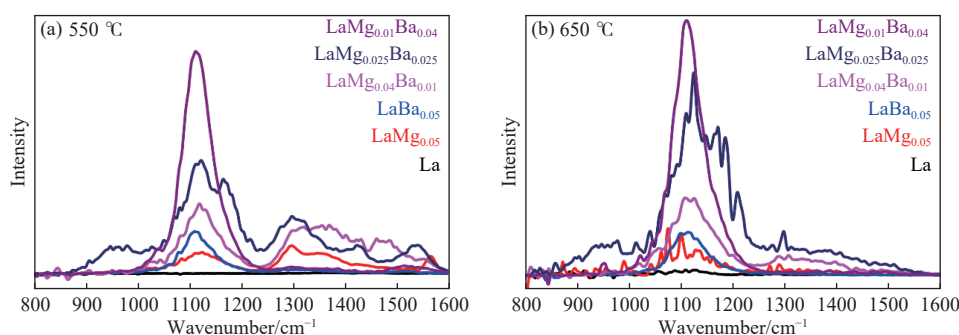


Fig. 9 *In situ* DRIFT spectra of Mg and Ba modified  $\text{La}_2\text{O}_3$  catalysts at (a) 550 °C and (b) 650 °C

As evidenced by the  $\text{O}_2/\text{H}_2$ -TPR results, the co-doping of Mg and Ba significantly enhances the activation and dissociation of  $\text{O}_2$  on the  $\text{La}_2\text{O}_3$  catalyst. Consequently, this co-doping strategy not only increases oxygen vacancies on the  $\text{La}_2\text{O}_3$  catalyst, thereby promoting oxygen activation, but also significantly elevates the concentration of superoxide species ( $\text{O}_2^-$ ) present on the catalyst surface. Combined with catalytic performance, the  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst exhibited the highest  $\text{C}_{2+}$  selectivity of 52.4%, while the  $\text{C}_{2+}$  selectivity of other catalysts was lower than 50% at 700 °C. This indicates that the presence of superoxide species ( $\text{O}_2^-$ ) is closely related to the  $\text{C}_{2+}$  selectivity.

## 2.4 Effect of surface oxygen species on OCM reaction

$\text{CH}_4/\text{O}_2$  pulse experiments were conducted to investigate the formation of surface oxygen species and their efficacy in activating  $\text{CH}_4$  to form  $\text{C}_2\text{H}_4$ . The variation in  $\text{CH}_4$  consumption under pulsed  $\text{O}_2$  at 700 °C is shown in Figure 10. Prior to  $\text{O}_2$  pulse, the catalyst was pretreated with  $\text{H}_2$  to remove adsorbed oxygen species. During the subsequent  $\text{O}_2$  pulses, oxygen species were progressively adsorbed, gradually establishing an equilibrium distribution between the surface and the bulk phase. All samples exhibited a similar two-stage response in  $\text{CH}_4$  signal intensity: as the number of  $\text{O}_2$  pulses increased, the  $\text{CH}_4$  signal intensity first gradually increased, and then tended to stabilize. The initial increase in  $\text{CH}_4$  signal intensity corresponds to the accumulation of surface active oxygen species on the catalyst, whereas the subsequent plateau of  $\text{CH}_4$  signal intensity indicates that adsorption equilibrium has been reached.  $\text{LaBa}_{0.05}$  required five  $\text{O}_2$  pulses to reach a stable  $\text{CH}_4$  signal, while La,  $\text{LaMg}_{0.05}$  and  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  require three  $\text{O}_2$  pulses to achieve equilibrium  $\text{CH}_4$  signal intensity. The Mg and Ba co-doped catalyst  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  achieved 86% of the equilibrium intensity in the  $\text{CH}_4$  signal during the first oxygen pulse, indicating that this catalyst promotes  $\text{O}_2$  activation and rapidly establishes adsorption equilibrium of oxygen species on both the catalyst surface and bulk phase.

The  $\text{C}_2\text{H}_4$  generation profiles of the catalysts following  $\text{O}_2$  pulses at 700 °C is shown in Figure 11. The signal intensity of  $\text{C}_2\text{H}_4$  also presented a trend of initial increase

followed by stabilization as the number of  $\text{O}_2$  pulses increased. A detailed comparison revealed that the  $\text{C}_2\text{H}_4$  signal for  $\text{LaBa}_{0.05}$  stabilized at the 4th  $\text{O}_2$  pulse, whereas that for  $\text{LaMg}_{0.05}$  required until the 5th pulse. Combined with *in situ* DRIFT (Figure 9) results, which showed a higher concentration of  $\text{O}_2^-$  species on  $\text{LaBa}_{0.05}$  than on  $\text{LaMg}_{0.05}$ , this further supports the governing role of superoxide species ( $\text{O}_2^-$ ) in the formation of  $\text{C}_{2+}$  products. Notably, no  $\text{C}_2\text{H}_4$  was detected for  $\text{LaBa}_{0.05}$  and  $\text{LaMg}_{0.05}$  catalysts in the first  $\text{O}_2$  pulse. This is attributed to the limited amount of  $\text{O}_2^-$  available during the first pulse, which favors the complete oxidation of  $\text{CH}_4$  to  $\text{CO}_2$ . The resulting  $\text{CO}_2$  is strongly adsorbed by the basic catalyst surface, explaining its absence in the gas-phase detection. It is worth noting that for the  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  catalyst, the  $\text{C}_2\text{H}_4$  signal intensity reached 81% of the equilibrium intensity during the first  $\text{O}_2$  pulse, which was significantly superior to other catalysts. This indicates that  $\text{LaMg}_{0.025}\text{Ba}_{0.025}$  facilitates the generation of superoxide species ( $\text{O}_2^-$ ) more readily, further verifying the *in situ* FT-IR results.

## 2.5 Activation of $\text{O}_2$ and $\text{CH}_4$ on $\text{La}_2\text{O}_3$ catalyst

The surface activation of  $\text{O}_2$  proceeds through reactive intermediates such as superoxide ( $\text{O}_2^-$ ) and dissociated oxygen species ( $\text{O}^-$  or  $\text{O}^{2-}$ )<sup>[46]</sup>. Mg doped  $\text{La}_2\text{O}_3$  promotes the activation of  $\text{O}_2$  on the catalyst surface. However, excessive  $\text{O}_2$  activation capacity led to the formation of a large quantity of dissociated oxygen species ( $\text{O}^-$ ), which promote the over-oxidation of  $\text{CH}_4$  to  $\text{CO}_x$  and consequently lower the  $\text{C}_{2+}$  selectivity. The Ba doped  $\text{La}_2\text{O}_3$  catalyst possesses a weaker  $\text{O}_2$  activation ability, yet the dopant interacts favorably with superoxide species ( $\text{O}_2^-$ ), stabilizing them on the surface. This results in a higher surface concentration of  $\text{O}_2^-$ , which selectively promotes the formation of  $\text{C}_{2+}$  products. When Mg and Ba are co-doped, the activation of  $\text{O}_2$  toward superoxide species ( $\text{O}_2^-$ ) is further enhanced, increasing the surface concentration of this selective oxygen species (Figure 12). Consequently, the Mg-Ba co-doped  $\text{La}_2\text{O}_3$  catalyst achieves superior  $\text{C}_{2+}$  selectivity (54.5%) at a relatively mild temperature of 700 °C, outperforming both singly doped  $\text{La}_2\text{O}_3$  catalysts.

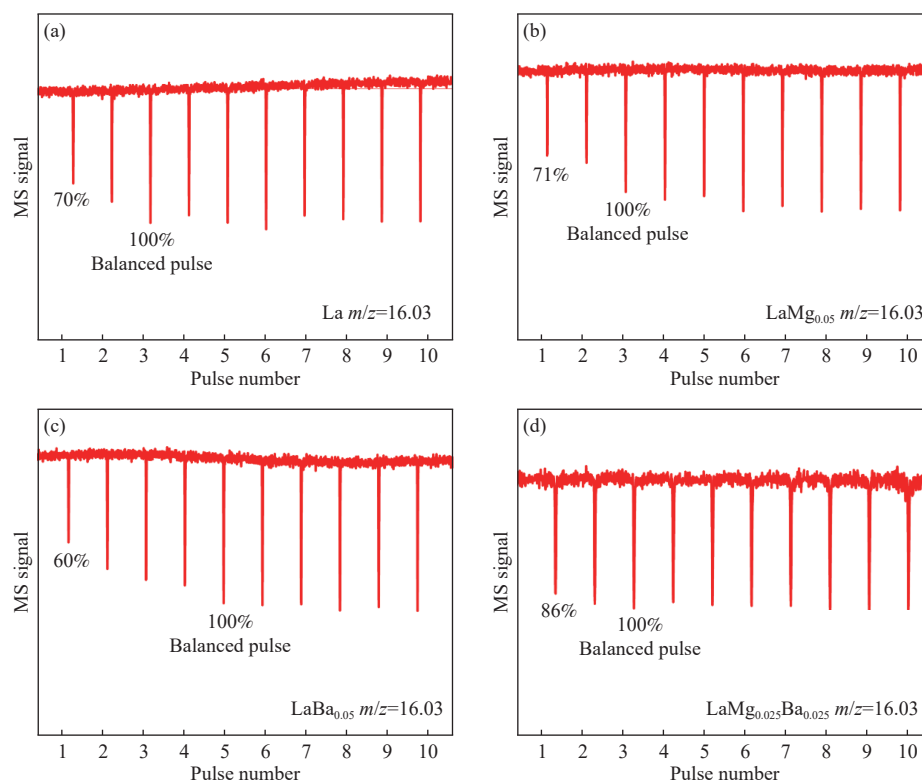


Fig. 10  $\text{CH}_4$  consumption signals from oxygen pulse experiments for Mg and Ba modified  $\text{La}_2\text{O}_3$  catalysts

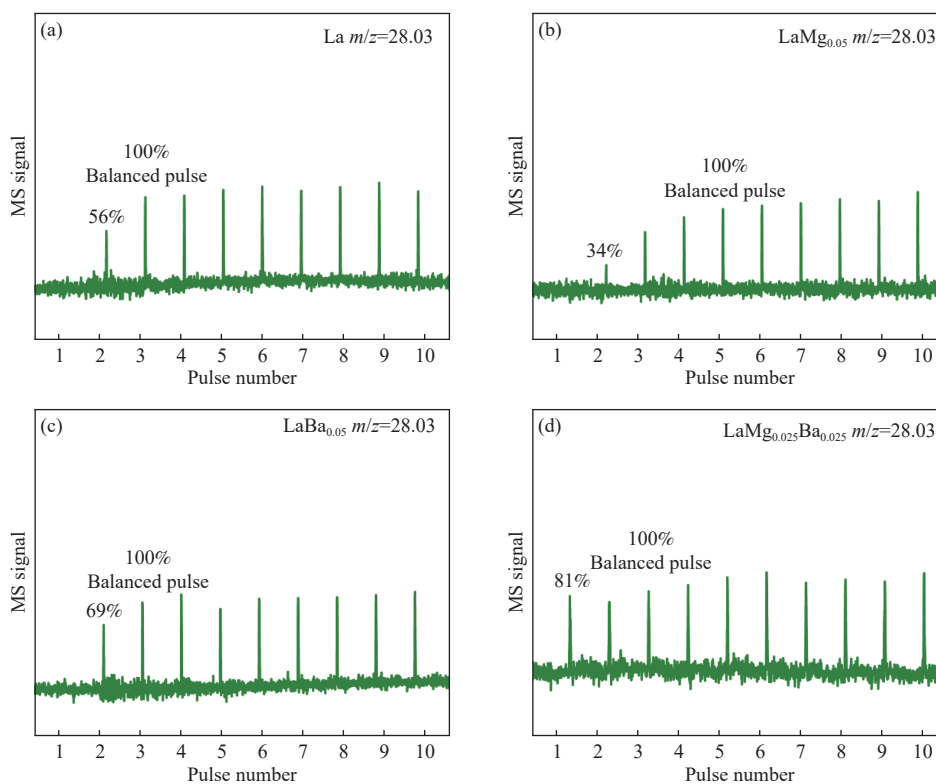


Fig. 11  $\text{C}_2\text{H}_4$  generation signals from oxygen pulse experiments for Mg and Ba modified  $\text{La}_2\text{O}_3$  catalysts

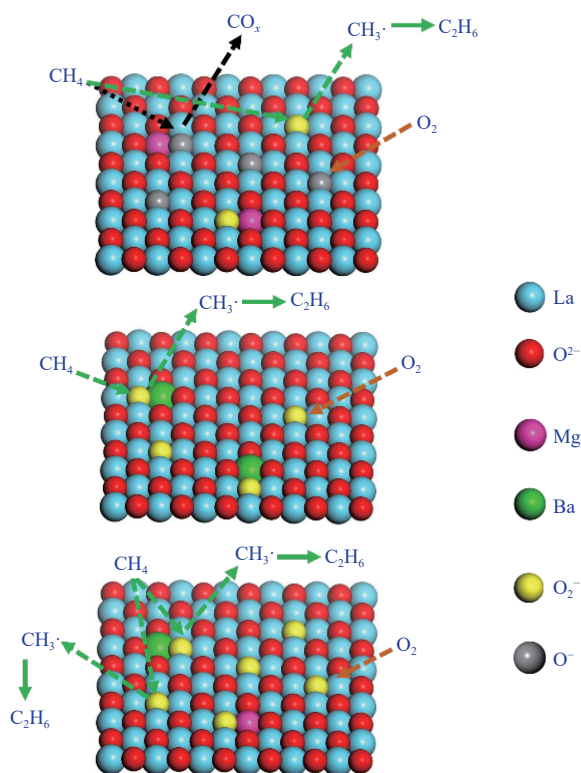


Fig. 12 OCM reaction process over Mg and Ba modified  $\text{La}_2\text{O}_3$  catalysts

### 3 Conclusion

In this study,  $\text{La}_2\text{O}_3$  catalysts single-doped with alkaline earth metals (Mg, Ca, Sr, Ba) and co-doped with Mg and Ba were prepared *via* a hydrothermal method, and their structure, catalytic performance, and oxygen species were systematically investigated. *In situ* DRIFTS revealed the presence of superoxide species ( $\text{O}_2^-$ ) on the surface of both Mg- and Ba-doped catalysts, with the co-doped system exhibiting a significantly more intense signal for the superoxide species  $\text{O}_2^-$ . This indicates a synergistic effect between Mg and Ba in promoting the formation and stabilization of these key reactive intermediates.  $\text{O}_2/\text{H}_2$ -TPR studies revealed that Mg and Ba co-doped  $\text{La}_2\text{O}_3$  catalysts exhibit superior  $\text{O}_2$  activation capabilities compared to those doped with Mg or Ba alone. Furthermore,  $\text{CH}_4/\text{O}_2$  pulse experiments revealed that the co-doped catalysts facilitate faster establishment of oxygen adsorption equilibrium, thereby enhancing  $\text{CH}_4$  activation and the subsequent formation of  $\text{C}_2$  products. This work establishes that co-doping  $\text{La}_2\text{O}_3$  with Mg and Ba represents an effective strategy for improving catalytic performance in the oxidative coupling of methane (OCM), primarily by modulating the generation and stabilization of key active oxygen species.

### Declaration of Competing Interest

The authors declare no conflict of interest.

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# Mg 和 Ba 共掺杂调控氧化镧表面氧物种以增强其在催化甲烷氧化偶联反应中的性能

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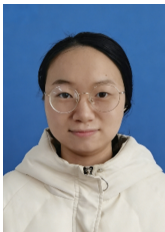
**摘要:** 采用水热法合成了 Mg、Ca、Sr 和 Ba 单掺杂改性及 Mg、Ba 共掺杂改性  $\text{La}_2\text{O}_3$  催化剂, 并评价了其在甲烷氧化偶联(OCM)反应中的催化性能。实验结果表明, Mg 改性  $\text{La}_2\text{O}_3$  催化剂表现出较高的  $\text{O}_2$  和  $\text{CH}_4$  活化能力, 但  $\text{C}_{2+}$  选择性较低。而 Ba 改性  $\text{La}_2\text{O}_3$  催化剂则表现出较高的  $\text{C}_{2+}$  选择性, 但反应活性较低。Mg 与 Ba 共掺杂改性  $\text{La}_2\text{O}_3$  催化剂, 能够在维持较高  $\text{C}_{2+}$  选择性的同时提升催化活性。当 Mg/Ba 物质的量比为 1:1 时, 该催化剂在 700 °C 条件下实现 29.5% 的  $\text{CH}_4$  转化率、54.5% 的  $\text{C}_{2+}$  选择性及 16.1% 的  $\text{C}_{2+}$  产物收率。通过  $\text{O}_2/\text{H}_2$ -TPR、原位 FT-IR 和  $\text{O}_2$  脉冲等方法对催化剂活化  $\text{O}_2$  和  $\text{CH}_4$  进行了研究。表征结果表明, Mg 和 Ba 共掺杂改性  $\text{La}_2\text{O}_3$  催化剂可在催化剂表面产生更多  $\text{O}_2^-$  物种, 从而显著提高  $\text{La}_2\text{O}_3$  催化剂的活性和选择性。

**关键词:** 甲烷氧化偶联;  $\text{La}_2\text{O}_3$ ; 镁和钡共掺杂;  $\text{O}_2^-$  物种

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