#### **Supplementary Materials**

SrSnO<sub>3</sub> perovskite versus Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlores for oxidative coupling of methane: deciphering the reactive sites difference

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#### **1. SUPPLEMENTARY EXPERIMENTAL INFORMATION**

### 1.1 CATALYST CHARACTERIZATION

Phase structures of the fresh and spent catalysts were determined through X-ray powder diffraction (XRD), which was performed using a PuXi XRD-3X with Cu target and K $\alpha$ -ray irradiation operating at 40 kV and 30 mA, with a 2° min<sup>-1</sup> rate from 10 to 80°. To determine the phase structure, the resulting XRD patterns were compared with PDF standard cards in jade 6.5.

The specific surface area of the fresh and spent catalysts was determined by using ST-08B instrument at 77 K liquid nitrogen temperature and calculated by BET method.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PerkinElmer PHI-1600 ESCA spectrometer. The XPS measurements were taken *in situ* using a high-pressure programmable cell (HPGC 300, Fermi Instruments). The binding energy of all XPS spectra was calibrated using the C1s peak (BEs= 284.6 eV). Thermo Avantage software was used to perform spectra fitting and all processing analysis. The O 1s spectra were fitted with the Lorentz-Gauss mix function (L:G = 2:8) after subtracting the modified Shirley (Smart) background. The FWHM (full widths at half maximum) of a single XPS oxygen peak ranged from 1.8 to 2.0 eV.

*In situ* Raman spectroscopy was conducted on a Renishaw inVia instrument under air conditions using a Linkam TS 1500 micro-size *in situ* cell. The laser excitation wavelength is 532 nm and the Raman shift recording range is 100-1000 cm<sup>-1</sup>.

Experiments including CH<sub>4</sub>-TPSR-MS, CH<sub>4</sub>-pulse test, CO<sub>2</sub>-TPD-MS, NH<sub>3</sub>-TPD-MS, O<sub>2</sub>-TPD-MS experiments, and <sup>18</sup>O<sub>2</sub><sup>-</sup>-pulse tests were conducted using a BelCata II apparatus equipped with a BelMass using quadruple as a mass analyzer. The outlet products (C<sub>2</sub>H<sub>4</sub> m/z=27, C<sub>2</sub>H<sub>6</sub> m/z=30 CO m/z=28 and CO<sub>2</sub> m/z=44) and desorption products (CO<sub>2</sub> m/z=44, NH<sub>3</sub> m/z=17, O<sub>2</sub> m/z=32, <sup>16</sup>O<sup>16</sup>O m/z =32, <sup>16</sup>O<sup>18</sup>O m/z =34, <sup>18</sup>O<sup>18</sup>O m/z =36 ) were measured instantaneously with the mass spectrometer system. Typically, a certain weight of the samples was pretreated at 800 °C under a pure He atmosphere (30 mL/min) for 30 min, which was then cooled to 50 °C. The sample pretreatment for all subsequent testing experiments is the same as this process.

For CH<sub>4</sub>-TPSR-MS tests in the presence of gaseous O<sub>2</sub>, the sample containing 200 mg after pretreatment, a flow of mixed gas of CH<sub>4</sub>/O<sub>2</sub>/He=4/1/5 (60 mL/min) was introduced, raising the temperature from 100 to 900 °C at a rate of 10 °C/min to record the relative mass signals. For CH<sub>4</sub>-TPSR-MS tests conducted in the absence of gaseous O<sub>2</sub>, the pretreated sample was exposed to a flow of mixed gas of CH<sub>4</sub>/He=4/6 (60 mL/min), The temperature was increased from 100 to 900 °C at a rate of 10 °C/min to collect the related mass signals.

For the CH<sub>4</sub> pulse test, after pretreatment, the test involves heating the sample with a rising rate of 10 °C/min to 800 °C. Then the sample is adsorbed with 10% O<sub>2</sub>-Ar saturation for 30 min. During the test, 1 mL of methane is pulsed continuously every 3 min, and the relevant mass spectrometry signals are recorded.

For the <sup>18</sup>O<sub>2</sub> pulse test, after pretreatment, the sample is heated at a rate of 10 °C/min to 800 °C, while pulsing 1mL of 10% <sup>18</sup>O<sub>2</sub>-Ar continuously every 3 min. The relevant mass spectrometry signals are recorded.

CO<sub>2</sub>-TPD experiments were performed on a BelCata II apparatus. Typically, 100 mg of catalyst was heated to 800 °C in high purity He flow with a rate of 30 mL/min and kept for 1 h to remove any possible impurities. Afterwards, the sample was cooled to 50 °C and exposed to CO<sub>2</sub> flow with a rate of 30 mL/min for 1 h to saturate the surface completely, which was followed by purging with a 30 mL min<sup>-1</sup> He (99.99%) flow to remove any physically adsorbed CO<sub>2</sub> for 30 min. After this, the catalyst was heated from 100 to 800 °C with a rate of 10 °C/min in the same feed. A TCD is employed to monitor the desorption CO<sub>2</sub>. The amount of CO<sub>2</sub> desorption of the samples was quantified using a 1 mL dosing loop.

For NH<sub>3</sub>- and O<sub>2</sub>-TPD-MS experiments, the sample (100 mg) was first treated and then exposed to 10% NH<sub>3</sub>-Ar or 10% O<sub>2</sub>-Ar flow at a rate of 30 mL min<sup>-1</sup> for 1 h at 50 °C. This was done to ensure that the surface of sample was completely saturated. After this, the sample was purged with a 30 mL min<sup>-1</sup> He (99.99%) for 30 min to remove any physically adsorbed NH<sub>3</sub> or O<sub>2</sub> for 30 min. After this, the catalyst was heated from 100 to 800 °C at a rate of 10 °C/min in the same feed. The amount of NH<sub>3</sub> or O<sub>2</sub> desorption of the samples was quantified using a 1 mL dosing loop. For CO<sub>2</sub>-TPD, according to their desorption temperature, they can be divided into weak basic sites (< 300 °C), moderate basic sites (300-600 °C), and strong basic sites  $(>600 °C)^{[1, 2]}$ . For NH<sub>3</sub>-TPD-MS, according to their desorption temperature, they can be divided into weak acidic sites (< 200 °C), moderate acidic sites (200-600 °C), and strong acidic sites (>600 °C)<sup>[3]</sup>. For O<sub>2</sub>-TPD-MS, according to their desorption temperature, they can be divided into loosely bounded oxygen (< 200 °C), chemisorbed oxygen (200-600 °C), and lattice oxygen (>600 °C)<sup>[4]</sup>.

H<sub>2</sub>-TPR was carried out using a FINESORB 3010C instrument equipped with TCD detector. Piror to the experiments, 50 mg of catalyst was calcined again in a high purity air flow at 120 °C for 30 min to remove any possible impurities. After purging with a 99.99% Ar flow at room temperature for 30 min, the H<sub>2</sub>-TPR experiment was started from room temperature to 800 °C with a rate of 10 °C/min in a 30 mL min<sup>-1</sup> 10% H<sub>2</sub>/Ar gas mixture flow, then recording the H<sub>2</sub>-TPR profiles.

FTIR spectra were performed on a Nicolet 5700 spectrophotometer using KBr disks. The recorded wavenumber is in the range of 4000 to 400 cm<sup>-1</sup>.

EPR technique was used to measure the catalysts. The catalysts were placed in liquid nitrogen of 77 K before recording the EPR signals. The EPR spectra were then recorded using a JEOL FA-200 EPR Spectrometer, which operated with a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz.

#### **1.2 REACTION PERFORMANCE EVALUATIONS FOR OCM REACTION**

The performance of the OCM reaction was evaluated in a fixed-bed quartz tube reactor with a length of 300 nm and an inner diameter of 6 mm. To prepare the reaction, 200 mg of catalyst was evenly mixed with quartz sand of equal weight and loaded into the reaction tube. It was then placed between layers of quartz wool. The reaction was carried out in the temperature range of 600-800 °C. To ensure stable kinetic data, all injections were taken for one hour before collecting steady-state data. The temperature of the quartz tube reactor was monitored by inserting a thermal couple into the reactor, with the headpoint touching the catalyst bed.

Three mass flow meters were used to control the reaction gas volume ratio of  $CH_4/O_2/Ar = 4/1/5$ . The total flow rate of the mixed gas is 60 mL/min, corresponding to a

weight hourly space velocity (WHSV) of 18000 mL•h<sup>-1</sup>•g<sup>-1</sup>. After removing the produced water vapor with a cold trap, the effluent mixed gases were analyzed by a GC9310 chromatograph equipped with a TDX-01 column and a TCD (for the separation of CO, CO<sub>2</sub> and CH<sub>4</sub>); and another GC9310II chromatograph equipped with a Propak Q column and an FID (for the separation of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>) in parallel. Based on the total carbon balance, the methane conversion (X<sub>CH4</sub>), oxygen conversion (X<sub>O2</sub>), C<sub>2</sub> selectivity (S<sub>C2</sub>) and C<sub>2</sub> yield (Y<sub>C2</sub>) were calculated by standard normalization in the following equations:

$$\mathbf{X}_{CH_4} = \frac{[2*(C_2H_4 + C_2H_6) + 3*(C_3H_6 + C_3H_8) + CO + CO_2]}{(CH_4)_{in}} \times 100\%$$
(1)

$$X_{02} = \frac{o_{2_{in}} - o_{2_{out}}}{o_{2_{in}}} \times 100\%$$
(2)

$$\mathbf{Sc}_{2} = \frac{2*(C_{2}H_{4}+C_{2}H_{6})}{2*(C_{2}H_{4}+C_{2}H_{6})+3*(C_{3}H_{6}+C_{3}H_{8})+C0+C0_{2}} \times \mathbf{100\%}$$
(3)

$$\mathbf{Y}_{\mathbf{C}_2} = \mathbf{X}_{\mathbf{CH}_4} \times \mathbf{S}_{\mathbf{C}_2} \times \mathbf{100\%} \tag{4}$$

### **1.3. Sn-O BOND FORCE CONSTANTS OF THE CATALYSTS**

The Sn-O bond force constants of the catalysts are calculated from FTIR spectra using the below equations<sup>[5]</sup>.

$$v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$
(5)

$$\mu = \frac{M_{Sn} \times M_0}{M_{Sn} + M_0} \tag{6}$$

v=IR wavenumber (cm<sup>-1</sup>) of the stretching vibration of metal-oxygen bonds,

c = speed of light (cm/s),

µ=the effective mass of the Sn cations and oxygen,

 $M_{Sn}$  = the atomic mass of Sn cations,

 $M_O$  = the atomic mass of oxygen (kg)<sup>[6]</sup>.



## 2. SUPPORTING FIGURES AND RELATED DESCRIPTIONS

Supplementary Figure 1. Catalytic performance of the ASnO<sub>3</sub> (A=Ca, Sr, Ba) perovskite catalysts OCM: (A) CH<sub>4</sub> conversion, (B) O<sub>2</sub> conversion, (C) C<sub>2</sub> selectivity, and (D) C<sub>2</sub> yield. Reaction conditions: CH<sub>4</sub>/O<sub>2</sub>/Ar = 4/1/5, GHSV=18000 mL•h<sup>-1</sup>•g<sup>-1</sup>.





Supplementary Figure 2. Catalytic performance of  $Ln_2Sn_2O_7$  (Ln=La, Pr, Nd) catalysts for OCM: (A) CH<sub>4</sub> conversion, (B) O<sub>2</sub> conversion, and (C) CO<sub>x</sub> selectivity. Reaction conditions: CH<sub>4</sub>/O<sub>2</sub>/Ar = 4/1/5, GHSV=18000 mL•h<sup>-1</sup>•g<sup>-1</sup>.

#### 2.1 X-RAY DIFFRACTION (XRD) PHASE ANALYSIS OF THE CATALYSTS

Supplementary Figure 3 (A) and (B) show the XRD results, which confirm the successful formation of two types of complex oxides with high crystallinity. All the samples exhibit their characteristic peaks, which have been identified their standard cards (CaSnO<sub>3</sub>: Jade, PDF#77-1797, SrSnO<sub>3</sub>: Jade, PDF#77-1798, BaSnO<sub>3</sub>: Jade, PDF#15-0780, La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>: Jade, PDF#13-0082, Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>: Jade, PDF#13-0184, Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>: Jade, PDF#13-0185). Furthermore, lattice parameters are determined using XRD Rietveld refinement (Supplementary Figure 4, Supplementary Table 1), while surface A/B atomic ratios are obtained using X-ray photoelectron spectroscopy (XPS) data (Supplementary Table 1). Supplementary Figure 5 shows the XRD patterns of the spent perovskite and pyrochlore catalysts. Evidently, none of the samples underwent structural changes. Supplementary Table 1 shows the specific surface areas of the fresh and spent catalysts, which have been determined using N<sub>2</sub>-BET. All the samples possess small specific surface areas, which showed an insignificant decrease after OCM.



**Supplementary Figure 3.** XRD patterns of the fresh catalysts (A) ASnO<sub>3</sub> (A=Ca, Sr, Ba) and (B) Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).



**Supplementary Figure 4**. The Rietveld refinement XRD patterns of (A) CaSnO<sub>3</sub>, (B) SrSnO<sub>3</sub>, (C) BaSnO<sub>3</sub>, (D) La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, (E) Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and (F) Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>.



**Supplementary Figure 5**. XRD patterns of the spent catalysts (A) ASnO<sub>3</sub> (A=Ca, Sr, Ba), (B) Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).



**Supplementary Figure 6**. Raman spectra of the fresh catalysts (A) ASnO<sub>3</sub> (A=Ca, Sr, Ba), (B) Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).



Supplementary Figure 7. In situ Raman spectra of CaSnO<sub>3</sub> and BaSnO<sub>3</sub> samples.



Supplementary Figure 8. In situ Raman spectra of La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> samples.

To investigate the phase transition of ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> at temperatures required for OCM, *in situ* Raman tests have been performed. The catalyst was pretreated at 800 °C under a pure He atmosphere for 30 min, which was then cooled to 50 °C, Then, the CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub>=4/1/5 mixture gas was introduced, and Raman spectra of catalysts were measured at 50, 600, 700, and 800 °C, respectively. The frequencies of Raman signals corresponding to ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> at room temperature are shown in Supplementary Table 2 and 3, respectively.

Supplementary Figure 7 (A) shows that in the Raman spectra of CaSnO<sub>3</sub>, some Raman active modes broaden, disappear, or shift to lower wavenumbers from 600 to 800 °C, thus testifying that they undergo lattice distortion at temperatures required for OCM. In theory, no Raman signals can be observed for regular cubic BaSnO<sub>3</sub>. In this study, as displayed in Figure 7 (B), the presence of Raman peaks indicate that the BaSnO<sub>3</sub> formed in this study is defective (i.e., Ba-site vacancy is coupled with an oxygen vacancy)<sup>[7]</sup>. With an increase in the reaction temperature, the mode at 560 cm<sup>-1</sup> corresponding to oxygen vacancies gradually disappears and other modes become smaller at 800 °C, indicating that the defective BaSnO<sub>3</sub> transforms to regular BaSnO<sub>3</sub>.

Supplementary Figure 8 (A) and (B) show that Raman peaks of La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlores mostly remain unchanged, except for the peak broadening caused by thermal lattice expansion at high temperatures. This indicates that pyrochlore compounds do not undergo phase transition or lattice distortion at temperatures required for OCM.



**Supplementary Figure 9**. Raman spectra of the spent catalysts (A) ASnO<sub>3</sub> (A=Ca, Sr, Ba), (B) Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).



Supplementary Figure 10. XRD pattern of SrSnO<sub>3</sub> after Long-term stability test.



**Supplementary Figure 11**. CO<sub>2</sub>-TPD profiles of (A) ASnO<sub>3</sub> (A=Ca, Sr, Ba), (B) Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd). NH<sub>3</sub>-TPD-MS profiles of (C) ASnO<sub>3</sub> (A=Ca, Sr, Ba), (D) Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).



**Supplementary Figure 12**. O<sub>2</sub>-TPD-MS profiles of (A) ASnO<sub>3</sub> (A=Ca, Sr, Ba), (B) Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).

As formerly reported, the acid-base and oxygen properties on a catalyst surface are closely related to its catalytic performance for OCM<sup>[2, 8-10]</sup>. In general, moderate and strong acidic sites promote deep hydrocarbon oxidation, while moderate and strong basic sites favor C<sub>2</sub> selectivity<sup>[11-14]</sup>. For reducible metal oxides, surface lattice O<sup>2-</sup> is the OCM-selective oxygen species; for non-reducible metal oxides, electrophilic oxygen species such as O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup>, and O<sup>-</sup> are the OCM-selective oxygen species<sup>[15-18]</sup>. To investigate the effect of these active sites on the catalytic performance for OCM, ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalysts have been characterized using CO<sub>2</sub>-TPD-MS, NH<sub>3</sub>-TPD-MS and O<sub>2</sub>-TPD-MS.

CO<sub>2</sub>-TPD-MS profiles of ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalysts are shown in Supplementary Figure 11 (A) and (B). the quantitative results have been demonstrated in Supplementary Table 4. For ASnO<sub>3</sub> perovskites, the number of moderate and strong basic sites exhibits the following order: BaSnO<sub>3</sub>>SrSnO<sub>3</sub>≈CaSnO<sub>3</sub>; this number is related to the basicity of the A-site cation oxide<sup>[19-21]</sup>. For Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the number of moderate and strong basic sites is also related to the basicity of the Ln-site cation oxide and exhibits the following order: La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> >Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> ≈Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub><sup>[12, 22]</sup>. Moreover, the number of basic sites favorable for the formation of C<sub>2</sub> hydrocarbons is higher in perovskites than that in pyrochlores. These results indicate that the A-site cation affects the number of moderate and strong basic sites in both types of composite oxides. NH<sub>3</sub>-TPD-MS profiles of ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> are shown in Supplementary Figure 11 (C) and (D). The quantitative results are demonstrated in Supplementary Table 5. For ASnO<sub>3</sub> perovskite, BaSnO<sub>3</sub> with the most abundant basic sites has almost no acidic sites, while the amount of acidic sites in CaSnO<sub>3</sub> and SrSnO<sub>3</sub> is relatively close. In addition, the acidic site amount of perovskites is lower than that of pyrochlores. For Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the number of acidic sites shows the following order: Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>>Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>>La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. Supplementary Table 1 shows that the A/B atomic ratios of both ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> are similar, indicating that the factors affecting their acidic and basic sites are not related to the enrichment of surface elements.

To investigate the oxygen properties of ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, O<sub>2</sub>-TPD experiments have been conducted. Supplementary Figure 12 and Supplementary Table 6 show that perovskites exhibit a higher desorption temperature and chemisorb more oxygen species than pyrochlores, indicating that both ASnO<sub>3</sub> and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> have different mechanisms for activating gas-phase oxygen. During OCM, active oxygen species of perovskites are generated through high-temperature lattice distortion<sup>[23]</sup>; thus, the onset temperatures of C<sub>2</sub> products are relatively high. Meanwhile, pyrochlore has intrinsic oxygen vacancies, which may generate reactive oxygen species; thus, the onset temperature of C<sub>2</sub> products is relatively low<sup>[24]</sup>. For ASnO<sub>3</sub>, the desorption amount of chemisorbed oxygen species exhibits the following sequence: SrSnO<sub>3</sub>>BaSnO<sub>3</sub>>CaSnO<sub>3</sub>; for Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the sequence is as follows: La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>< Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>< Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. Moreover, La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> clearly exhibits the desorption peaks of lattice oxygen species.

The analysis of acid-base properties reveals that for ASnO<sub>3</sub>, the number of moderate and strong basic sites exhibits the following order: BaSnO<sub>3</sub>>SrSnO<sub>3</sub>>CaSnO<sub>3</sub>. Meanwhile, the number of acidic sites is inversely proportional to the number of basic sites. Theoretically, the C<sub>2</sub> selectivity of ASnO<sub>3</sub> should exhibit the following order: BaSnO<sub>3</sub>>SrSnO<sub>3</sub>>CaSnO<sub>3</sub>. O<sub>2</sub>-TPD-MS results indicate that the amount of chemisorbed oxygen ASnO<sub>3</sub> obey the following sequence: SrSnO<sub>3</sub>>BaSnO<sub>3</sub>>CaSnO<sub>3</sub>. Theoretically, since BaSnO<sub>3</sub> has Schottky defects and intrinsic oxygen vacancies, it can generate a high amount of chemisorbed oxygen species. Meanwhile, SrSnO<sub>3</sub> possesses abundant chemisorbed oxygen species because it undergoes a symmetry change at high temperatures, which causes lattice distortion and generates oxygen vacancies. On one hand, since the number of moderate and strong basic sites of SrSnO<sub>3</sub> is higher, it exhibits a better catalytic performance at high temperatures. On the other hand, BaSnO<sub>3</sub> transitions from a defective perovskite to a regular perovskite when the temperature increases, which leads to the destruction of its intrinsic oxygen vacancies and results in a better low-temperature catalytic performance and poorer high-temperature catalytic performance. In addition, BaSnO<sub>3</sub> is dominated by strong basic sites and its surface basicity is too strong, which leads to the formation of stable carbonates at high temperatures during OCM that are difficult to desorb and thus block the active sites. Meanwhile, CaSnO<sub>3</sub>, does not undergo lattice distortion at high temperatures; therefore, its catalytic performance is moderate.

It has been reported that coordination unsaturated metal cations (acidic sites) are known to chemically adsorb methyl radicals, ethyl radicals, and the ethylene formed during OCM. Consequently, a series of reactive oxygen species is generated via the activation of gas-phase oxygen, after which  $CO_x$  products are formed<sup>[3]</sup>. Therefore, the synergistic effect of acidic sites and reactive oxygen species on the catalyst surface can lead to the generation of deep oxidation products. Although Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> surfaces exhibit a lower number of basic sites than ASnO3 surfaces, they exhibit more acidic sites than ASnO<sub>3</sub>. Theoretically, among  $Ln_2Sn_2O_7$  samples, CH<sub>4</sub> conversion exhibits the following order: Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>>Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>>La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. O<sub>2</sub>-TPD-MS results show that the number of chemisorbed oxygen species exhibits the following order:  $La_2Sn_2O_7 < Pr_2Sn_2O_7$ <Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. This result is consistent with our previous findings; that is, with a decrease in the ionic radius of the A-site cation of pyrochlore, lattice disorder gradually increases along with the number of surface active oxygen species<sup>[25]</sup>. For La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, both the number of acidic sites and the chemisorbed oxygen amount are the lowest; therefore, its CH<sub>4</sub> conversion is the lowest. For Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the number of acidic sites is the highest, the chemisorbed oxygen amount is intermediate between that of the other two, and CH<sub>4</sub> conversion is also intermediate. For Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the chemisorbed oxygen amount is the highest, the number of acidic sites is intermediate between that of the other two, and CH<sub>4</sub> conversion is the highest. These results indicate that for Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlores, the

synergistic effect of oxygen and acidic sites leads to deep methane oxidation, with the oxygen sites playing a more significant role.



**Supplementary Figure 13**. (A) XRD patterns of the SrSnO<sub>3</sub> and Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalysts after H<sub>2</sub>-TPR reaction. (B) EPR spectra of the spent SrSnO<sub>3</sub> and Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalysts.

# **3. SUPPORTING TABLES**

Samples	Crystalline	Lattice p	arameters			Specifi	с	A/B atomic
	phase					surface areas		ratio
					$(m^{2}/g)$			
		a (Å)	b (Å)	c (Å)	α, β, γ (°)	Fresh	Spent	
CaSnO <sub>3</sub>	orthorhombic	5.553	5.663	7.895	90, 90, 90	5.0	4.8	0.98
SrSnO <sub>3</sub>	orthorhombic	5.710	5.723	8.067	90, 90, 90	6.4	5.9	0.94
BaSnO <sub>3</sub>	cubic	4.119	4.119	4.119	90, 90, 90	7.2	6.8	0.93
$La_2Sn_2O_7$	cubic	10.710	10.710	10.710	90, 90, 90	12.0	11.8	0.94
$Pr_2Sn_2O_7$	cubic	10.611	10.611	10.611	90, 90, 90	11.2	11.0	0.92
$Nd_2Sn_2O_7\\$	cubic	10.576	10.576	10.576	90, 90, 90	10.5	9.9	0.95

# Supplementary Table 1 Physico-chemical properties of the composite oxide catalysts.

# Supplementary Table 2 Frequencies (cm<sup>-1</sup>) of the Raman active modes for ASnO<sub>3</sub>

(A=Ca.	Sr.	Ba).
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CaSnO <sub>3</sub> <sup>[26]</sup>		SrSnO <sub>3</sub> <sup>[27]</sup>		BaSnO <sub>3</sub> <sup>[7]</sup>	
Frequencies	Assigned mode	Frequencies	Assigned	Frequencies	Assigned
$(cm^{-1})$		(cm <sup>-1</sup> )	mode	$(cm^{-1})$	mode
178	$A_g(3)$ with rotations around (010)	151	$B_{2g}$	143	-
276	Ag(5) with rotations around (101)	170	$A_{g}$	414	-
358	Sn-O torsional modes	223	A <sub>g</sub> Mode of the Sn-O-Sn groups along the c axis	560	Oxygen vacancy
443	Sn-O torsional modes	259	A <sub>g</sub> O-Sn-O bending in the ab plane and Sn-O-Sn scissoring perpendicular to the c axis	835	CO3 <sup>2-</sup>
468	Stretching modes of Sn-O	403	-		
642	Stretching modes of SnO <sub>3</sub>	575	Sn-O <sub>3</sub> vibration band		

Assigned mode	$La_2Sn_2O_7^{[28]}$	$Pr_2Sn_2O_7^{[29]}$	Nd <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub> <sup>[30]</sup>
	Frequencies (cm <sup>-1</sup> )	Frequencies (cm <sup>-1</sup> )	Frequencies (cm <sup>-1</sup> )
Eg	296	300	305
Ag	495	500	501
F <sub>2g</sub>	330	-	-
$F_{2g}$	401	392	412
$F_{2g}$	520	-	-
$F_{2g}$	704	695	-

Supplementary Table 3 Frequencies (cm<sup>-1</sup>) of the Raman active modes for Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>

**Supplementary Table 4** CO<sub>2</sub>-TPD quantification results of ASnO<sub>3</sub> (A=Ca, Sr, Ba) and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).

Samples	Weak	Moderate+Strong	Total
	(µmol/m²)	(µmol/m²)	$(\mu mol/m^2)$
CaSnO <sub>3</sub>	-	0.08	0.08
SrSnO <sub>3</sub>	-	0.10	0.10
BaSnO <sub>3</sub>	-	0.15	0.15
$La_2Sn_2O_7$	0.02	0.01	0.03
$Pr_2Sn_2O_7$	0.02	0.01	0.01
Nd <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	-	0.01	0.01

Supplementary Table 5 NH<sub>3</sub>-TPD-MS quantification results of ASnO<sub>3</sub> (A=Ca, Sr, Ba)

and Ln <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	(Ln=La,	Pr, Nd).
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Samples	Weak (mmol/m <sup>2</sup> )	Moderate+Strong (mmol/m <sup>2</sup> )	Total (mmol/m <sup>2</sup> )
CaSnO <sub>3</sub>	-	0.01	0.01
SrSnO <sub>3</sub>	-	0.01	0.01
BaSnO <sub>3</sub>	-	-	-
$La_2Sn_2O_7$	-	0.01	0.01
$Pr_2Sn_2O_7$	-	0.07	0.07
$Nd_2Sn_2O_7$	-	0.04	0.04

100~400 °C >600 °C Samples 200~600 °C Total  $(\mu mol/m^2)$  $(\mu mol/m^2)$  $(\mu mol/m^2)$  $(\mu mol/m^2)$ 0.12 CaSnO<sub>3</sub> 0.12 --0.16 0.16 SrSnO<sub>3</sub> --BaSnO<sub>3</sub> 0.06 0.06 \_ \_ 0.02 0.02  $La_2Sn_2O_7$ 0.01  $Pr_2Sn_2O_7$ 0.01 0.01 -\_  $Nd_2Sn_2O_7\\$ -0.03 -0.03

**Supplementary Table 6** O<sub>2</sub>-TPD-MS quantification results of ASnO<sub>3</sub> (A=Ca, Sr, Ba) and Ln<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> (Ln=La, Pr, Nd).

Supplementary Table 7 Refined Sn-O bond lengths of SrSnO<sub>3</sub> and Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>.

Samples	Sn-O bond lengths	Samples	Sn-O bond lengths
	(Å)		(Å)
SrSnO <sub>3</sub>	Sn-O1 2.056 (5)	$Nd_2Sn_2O_7$	Sn-O 2.083 (6)
	Sn-O1 2.056 (5)		
	Sn-O2 2.054 (5)		
	Sn-O2 2.054 (5)		
	Sn-O3 2.045 (6)		
	Sn-O3 2.045 (6)		

Supplementary Table 8 The electronegativity values of elements in this study.

Sr	Nd	Sn	0
0.95	1.14	1.96	3.44

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