

Supporting Information

Monodisperse Sr-La₂O₃ hybrid nanofibers for oxidative coupling of methane to synthesize C₂ hydrocarbons

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1. Experimental

Preparation of Sr-La₂O₃ hybrid nanofibers

La₂O₃ nanofibers were prepared by precipitation method. In a typical process, ammonia was added, dropwise, to 0.1 mol/L La(NO₃)₃ solution, and stirred for one hour to obtain a white gel. After washed by nanopure water for 3 times, the gel was suspended in nanopure water and heated at 105 °C for 24 hours. The lanthanum hydroxide was isolated by centrifugation and suspended in ethanol. After dried at 65 °C until all ethanol was removed, the lanthanum hydroxide nanofibers were obtained. The lanthanum hydroxide nanofibers prepared above were calcined at 690 °C for 4 hours to obtain the La₂O₃ nanofibers.

Sr-La₂O₃ nanofibers were synthesized by incipient wetness impregnation. In a typical procedure, different amounts of Sr(NO₃)₂ were dissolved in nanopure water, and then added in a drop-wise manner to a certain amount of La(OH)₃ nanofibers prepared above until a paste was obtained. The samples were then dried at 65 °C and calcinated at 800 °C for 4 h to obtain the Sr-La₂O₃ nanofibers. K-La₂O₃, Ba-La₂O₃, and Ca-La₂O₃ nanofibers were prepared by similar method with Sr-La₂O₃ nanofibers.

OCM test

The catalytic measurements were carried out in a laboratory quartz fixed bed reactor (9 mm inner diameter, 14 mm outer diameter, 50 cm length). Each catalyst was pressed under 30 MPa, then crushed and sieved to a size range of 40-80 mesh. For loading the reactor, 0.2 g of the sieved catalyst was mixed with 0.8 g quartz sand, and then placed in the quartz reactor tube between two pieces of quartz wool. Before the OCM reaction, the catalysts were pretreated under N₂ (flow rate: 30 mL/min) at 800 °C for 2 h and then switched to the reactants consisting 75 % CH₄ and 25% O₂ (flow rate: 240 mL/min) when the feed temperature dropped to 400 °C. A cold trap was placed at the outlet of the quartz tube to separate any condensed water vapor from the reaction products. The non-condensable gases (H₂, CO, CO₂, CH₄, O₂, C₂H₆ and C₂H₄) were then dried by the CaCl₂ column, and analyzed on-line by a micro gas chromatograph (3000 Micro GC; Inficon) equipped with two thermal conductivity detectors (TCD), one Molecular sieve 5A and one Plot U columns. Quantitative analyses of products were using external standard method.

Typically, > 99 % of carbon mass balance was achieved. CH₄ conversion, C₂ selectivity, C₂ yield and the selectivity of other carbon products were calculated on the basis of the following equation:

$$\begin{aligned} CH_4 \text{ Conversion} \quad X_{CH_4} &= \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \\ C_2 \text{ Selectivity} \quad S_{C_2} &= \frac{2(x_{C_2H_4} + x_{C_2H_6})}{x_{CO} + x_{CO_2} + 2(x_{C_2H_4} + x_{C_2H_6})} \times 100\% \\ C_2 \text{ Yield} \quad Y_{C_2} &= X_{CH_4} \cdot S_{C_2} \end{aligned}$$

Characterization

The X-ray powder diffraction (XRD) of the samples was carried out on a Rigaku Ultima X-ray diffractometer using Cu K α radiation, scanning in the range 5-90°, with a scan rate of 4°/min. The morphology and composition of the samples were examined by Hitachi S-4800 scanning electron microscope (SEM) combined with

Bruker quanta 400 Energy Dispersive X-ray Fluorescence Spectrometer (EDS). Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 S-TWIN transmission electron microscope at an operating voltage of 200 kV, equipped with a Gatan Orius CCD camera. X-ray photoelectron spectra (XPS) were recorded on a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. For all the computer fits, the XPS peaks were assumed to have 80% Gaussian plus 20% Lorentzian peak shape. CO₂ temperature-programmed desorption measurements were performed on Micromeritics AutoChem II 2920 instrument connected to a MKS cirrus mass spectrum. The catalyst power (150 mg) was heated a He flow from 60 to 800 °C at a heating rate of 10 °C /min and keep for 60 min at 800 °C, and then cooled to 60 °C. The CO₂ was injected at 60 °C for 60 min. The CO₂ was switched to He for 60 min, and the CO₂-TPD results were recorded at a heating rate of 10 °C /min. The CO₂ desorbed was measured quantitatively by mass spectrum. Thermogravimetric (TG) experiments were performed under 30 mL/min Air (20 % O₂ + 80 % N₂) with a heating rate of 5 °C/min on a Netzsch STA 449 F3 thermoanalyzer.

Supporting Figures

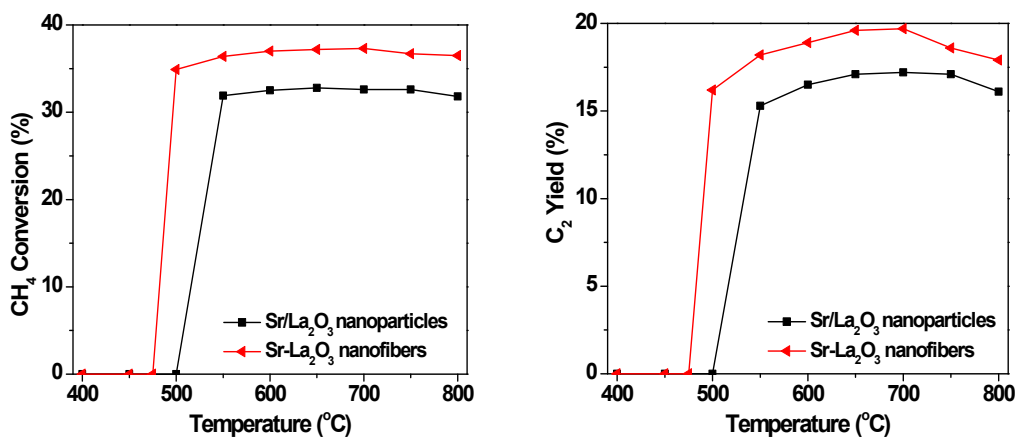


Figure S1. Comparison of OCM test for Sr-La₂O₃ nanofibers and Sr/La₂O₃ nanoparticles. (The synthesis of La₂O₃ nanoparticles are referred to ref.18)

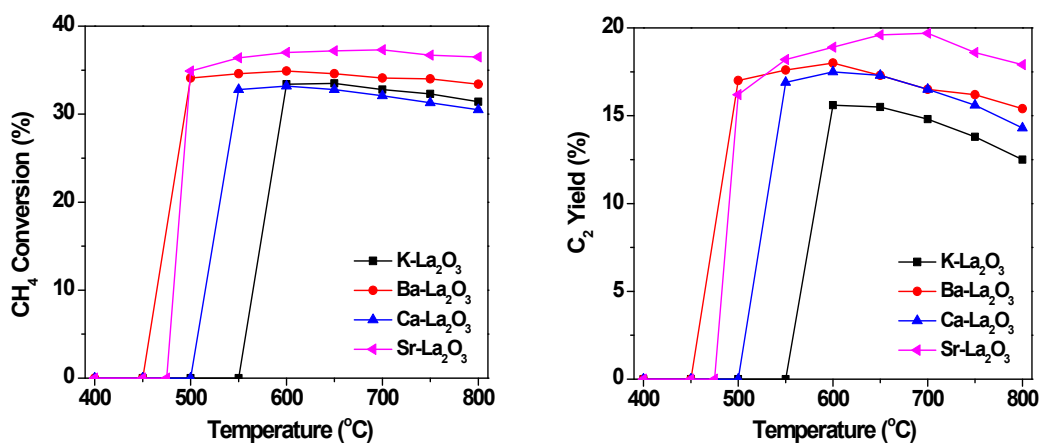


Figure S2. Comparison of OCM test for K-La₂O₃ (5 wt% K), Ba-La₂O₃ (3.8 wt% Ba), Ca-La₂O₃ (8.6 wt% Ca) and Sr-La₂O₃ (8.6 wt% Sr) nanofibers for OCM reaction.

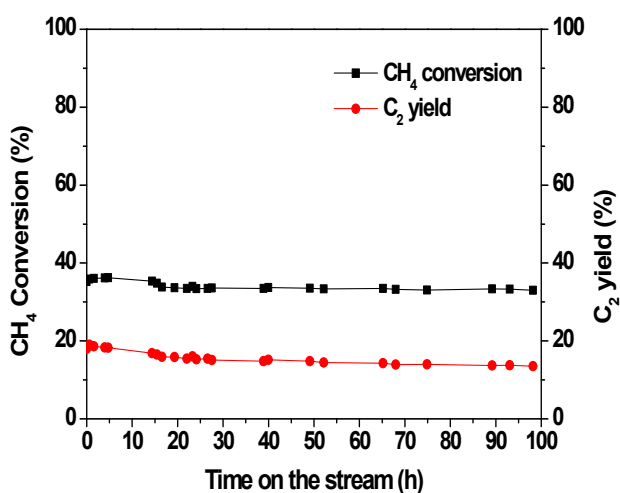


Figure S3. The stability of Sr-La₂O₃ for OCM reaction under below condition: reaction time = 100 h, T = 650°C, P = 1 atm, CH₄/O₂ = 3, GHSV = 72000 ml·g⁻¹·h⁻¹.

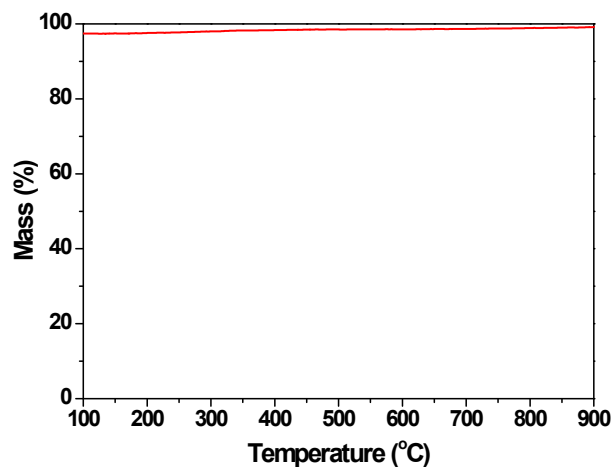


Figure S4. TG pattern of spent 8.6 wt% Sr-La₂O₃ nanofibers under 30 mL/min Air (20 % O₂ + 80 % N₂).

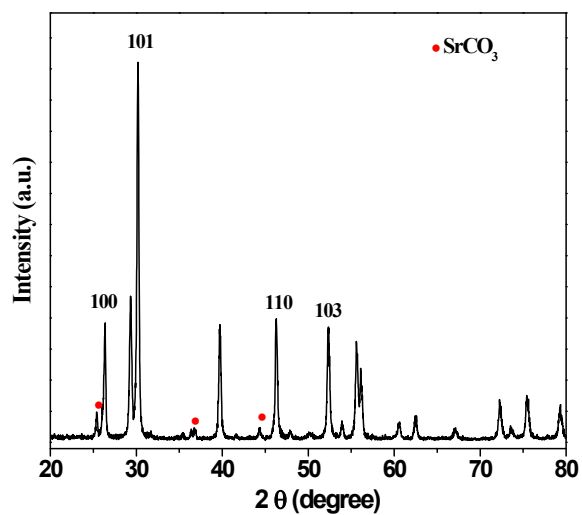


Figure S5. XRD pattern of spent 8.6 wt% Sr-La₂O₃ nanofibers

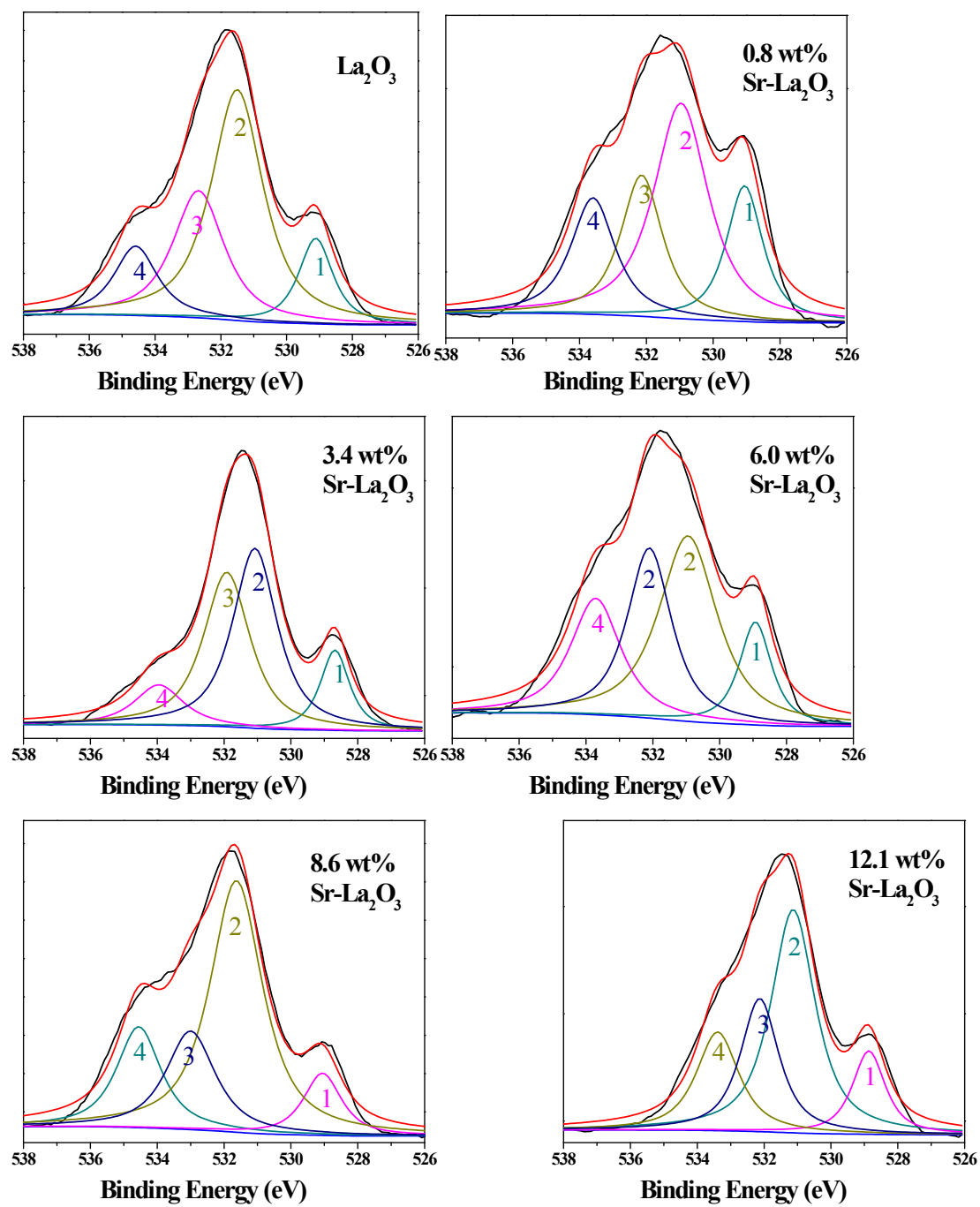


Figure S6. O1s binding energy spectra of fresh catalysts.