Electronic Supplementary Information

Preparation of La$_2$Zr$_2$O$_7$ composite oxides with fluorite/pyrochlore phases by excluding element influences for catalyzing oxidative coupling of methane

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1. Supplementary Experimental Information

1.1 Catalyst characterization

The crystalline structure of the catalyst before and after OCM was analyzed using a Bruker AXS D8 Focus X-ray diffractometer system, which was operated at 40 KV and 30 mA using a Cu target and Kα-ray irradiation. Scans were collected in the 2θ range of 10–80° with a step of 2°/min, and the crystalline structure was identified by using the PDF standard cards in Jade 6.5.

The specific surface area of the catalyst was measured using the ST-08B instrument at 77 K via the Brunauer, Emmett, and Teller method.

X-ray photoelectron spectroscopy (XPS) tests were conducted using a PerkinElmer

PHI-1600 ESCA spectrometer with a single MgKα X-ray source, which was operated at 300 W and 15 kV. The binding energies of all the samples were calibrated with the C1s peak of contaminant carbon (BE = 284.6 eV). The XPS peak fitting of all samples was performed using the Thermo Avantage software. O 1s spectra were fitted and deconvoluted with the Lorentz-Gauss mix function (L:G = 2:8) after subtracting the modified Shirley/Smart background. The full width at half maximum of a single XPS oxygen peak ranged between 1.8 and 2.0 eV.

Fourier transform infrared (FTIR) spectra from 4000 to 400 cm^{-1} were acquired using a Nicolet 5700 spectrophotometer with KBr disks. In situ diffuse reflectance FTIR spectroscopy (DRIFTS) experiments were performed on a Bruker Vertex spectrometer equipped with a mercury-cadmium-tellurium detector chilled in liquid nitrogen. A micro-size in situ DRIFT cell equipped with KBr windows was also used; 50 mg of the catalyst powder was pretreated first at 500 °C for 1 h under a 99.9% Ar flow rate of 30 mL/min, after which it was cooled to the target temperature. At this stage, background spectra were collected at a resolution of 4 cm^{-1} by accumulating 64 scans in a 30 mL/min Ar flow. All the DRIFTS spectra in this study were obtained by subtracting the corresponding background spectrum. The spectra were recorded continuously for each series of *in situ* experiments until the reaction reached equilibrium at around 30 min.

Raman spectra of the catalysts were obtained using a Renishaw inVia instrument under a laser excitation wavelength of 532 nm. In situ Raman spectra were acquired using the same instrument equipped with a Linkam TS 1500 micro-size in situ cell. The Raman shift ranged between 100 to 1000 cm^{-1}.

CH_4-TPSR-MS (temperature programmed surface reaction-mass spectrometry), CH_4-pulse reaction, and $^{18}O_2$ pulse reaction were performed on a BelCata II apparatus equipped with a BelMass by using quadruple as a mass analyzer. The mass spectrometry signals of outlet products (C_2H_4 m/z=27, C_2H_6 m/z=30 CO m/z=28 and CO_2 m/z=44) and oxygen isotopes ($^{18}O_2$ m/z=36, $^{18}O^{16}O$ m/z=34 and $^{16}O_2$ m/z=32) were measured instantaneously with the mass spectrometer system; 200 mg of a single sample was pretreated at 800 °C under a pure He atmosphere (30 mL/nin) for 30 min, after which it was cooled to 50 °C. The sample pretreatment process for all subsequent

testing experiments was the same.

To perform CH_4-TPSR-MS in the presence or absence of gaseous O_2, the sample (200 mg) was subjected to pretreatment, a flow of mixed gas (either CH_4:O_2:He=4:1:5 (60 mL/min) or CH4 :He=4: 5 (60 mL/min)) was introduced, and the temperature was increased from 50 to 900 °C at a rate of 10 °C/min.

For the CH_4 pulse test, the perpetrated sample was heated at a rate of 10 °C/min to 750 °C and subjected to adsorption in a 10% O_2/Ar gas mixture until saturation was achieved (for 30 min). Subsequently, 1 mL of methane was pulsed continuously every 3 min, and the relevant mass spectrometry signals were recorded. For the $^{18}O_2$ pulse reaction, the pretreated sample was heated at a rate of 10 °C/min to 750 °C, 1 mL of 3% $^{18}O_2$/He was added for each pulse, and the relevant mass spectrometry signals were obtained.

The ultraviolet-visible (UV-vis) absorbance spectra of the catalysts were acquired from 200 to 800 nm using a Cary 100 UV−visible spectrophotometer (Agilent). The emission spectra of the samples were obtained using a Xe 900 fluorescence spectrometer (Edinburgh, UK).

Electron paramagnetic resonance (EPR) spectra were obtained on a JEOL FA-200 EPR spectrometer, which was operated at a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz. The samples were first pretreated in an oxygen atmosphere at 750 oC for 1 h and then cooled to room temperature. Then, the samples were evacuated and placed in liquid nitrogen at -196 °C prior to collecting the EPR signals.

CO_2-temperature programmed desorption (TPD) was performed on an Autochem-II 2920 apparatus equipped with a TCD detector; 0.1 g of the sample was loaded into the quartz reactor, sandwiched between layers of quartz wool, and pretreated at 800 °C under a pure He flow (30 mL/min) for 30 min. Subsequently, the temperature was reduced to 50 °C and a 30 mL/min CO_2 flow was introduced until adsorption saturation was achieved (1 h). Again, a pure He (30 mL/min) flow was introduced for 1 h to remove the physically adsorbed CO_2 content, and the reactor temperature was increased from 50 to 800 °C at a rate of 10 °C/min. The amount of CO_2 desorbed was measured

using a $MgCO_3$ (99.9 %) standard, which undergoes completely decomposition at around 600 oC according to the following stoichiometric equation: $MgCO_3 = MgO + CO_2 \uparrow$.
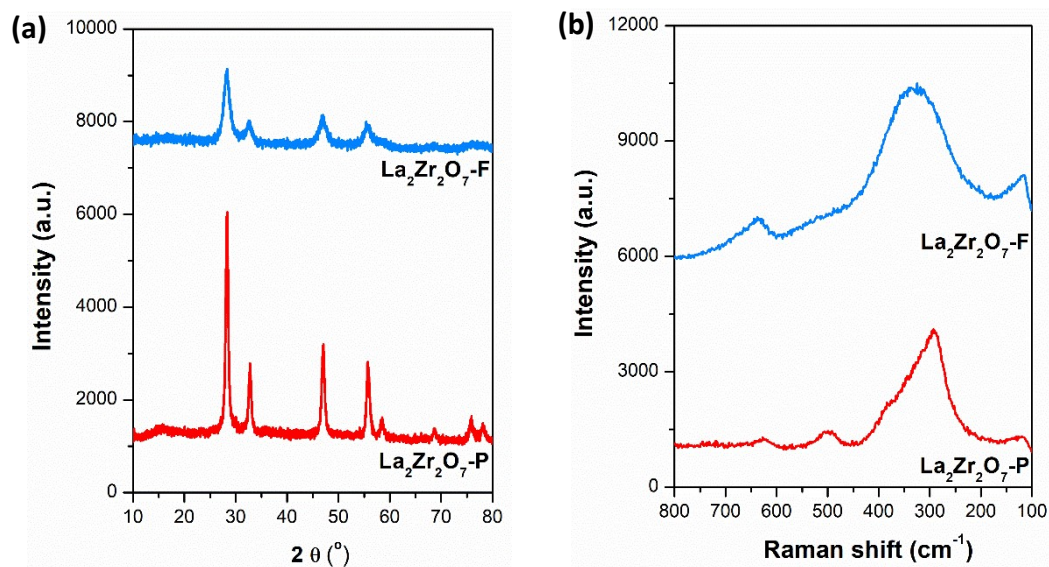
2. Supplementary Results

Fig. S1 (a) XRD patterns of the spent catalysts, (b) Raman spectra of the spent catalysts.