

Electronic Supplementary Information

**Low-temperature catalytic chemical looping dry reforming of methane over  
Ru/La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>**

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## Experimental Section

### Preparation of oxygen carriers

For this study,  $\text{La}_2\text{Ce}_2\text{O}_7$  (denoted as LCO) and  $\text{CeO}_2$  were synthesised using a complex polymerisation method. After the stoichiometric precursors (Kanto Chemical Co. Inc.) of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (when used) were dissolved in pure water, we added excess citric acid and ethylene glycol (Kanto Chemical Co. Inc.) with a molar ratio of metal ion: citric acid: ethylene glycol = 1: 3: 3 to the solutions. The solutions were dried with stirring at 573 K. Subsequently, the obtained solid mixtures were moved into a muffle furnace, pre-calcined at 673 K for 2 h ( $10 \text{ K} \cdot \text{min}^{-1}$  heating rate), and calcined at 1123 K for 10 h ( $20 \text{ K} \cdot \text{min}^{-1}$  heating rate). Finally, the target materials were prepared.

Different weight percentages of Ru-loaded  $\text{La}_2\text{Ce}_2\text{O}_7$  (denoted as  $x\text{Ru/LCO}$ ;  $x = 0.5, 1, 3$  and  $5$ ) oxygen carriers were prepared using the wet impregnation method. First,  $\text{La}_2\text{Ce}_2\text{O}_7$  and  $\text{Ru}(\text{acac})_3$  (Kanto Chemical Co. Inc.) were added to 10 mL ethanol and were then stirred for 2 h using a rotary evaporator at room temperature. Subsequently, the solutions were dried with stirring at 573 K and then moved into the oven at 393 K overnight. Subsequently, the obtained solid mixtures were moved into the muffle furnace and were calcined at 1123 K for 10 h. The prepared as-made materials were crushed and sieved to have a particle range of 355–500  $\mu\text{m}$  for use in redox tests.

### Characterisations

Using a BELMASS II mass spectrometer,  $\text{CH}_4$  temperature-programmed reduction ( $\text{CH}_4$ -TPR) was measured on a fixed bed reactor (as presented in Fig. S1). A 200 mg portion of the oxygen carrier was pretreated at 673 K for 30 min with  $\text{H}_2$  ( $\text{H}_2$  :  $\text{Ar} = 1 : 4$ ;  $50 \text{ mL} \cdot \text{min}^{-1}$  total flow rate) and was cooled to lower than 373 K. The analysis was conducted in a mixture of 10 vol%  $\text{CH}_4$  in  $\text{Ar}$  ( $100 \text{ mL} \cdot \text{min}^{-1}$ ) from 373 to 1173 K at  $10 \text{ K} \cdot \text{min}^{-1}$ .

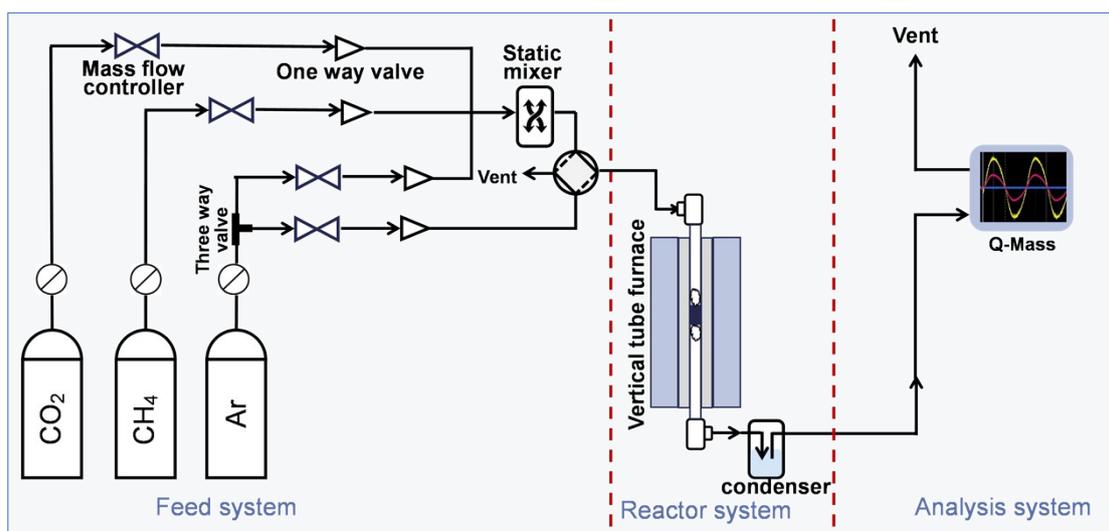


Fig. S1 The experimental system for DRM-CL performance tests by detecting the gas phase.

Powder X-ray diffraction (XRD) measurements were conducted using an X-ray diffractometer (Smart Lab-III; Rigaku Corp.) with Cu- $K\alpha$  radiation at 40 kV and 40 mA. Raman spectra were measured on an NRS-4500 (Jasco Corp.) with an excitation laser wavelength of 532 nm. The specific surface area was calculated from the nitrogen adsorption isotherm at 77 K using the Brunauer–Emmett–Teller (BET) method (Gemini VII 2390a; Micromeritics Instrument Corp.). The morphology and element distribution of 1Ru/LCO were investigated using a scanning transmission electron microscope with an energy-dispersive X-ray spectrometer (STEM-EDX, JEM 2100F (UHR); JEOL) operated at 200.0 kV.

X-ray photoelectron spectroscopy (XPS) measurements were taken using an instrument (VersaProbe4; Ulvac-PHI Inc.) equipped with a pre-treatment chamber. The samples underwent a sequential pre-treatment process in the chamber, including reduction at 673 K for 30 min with 20 vol%  $H_2$ , subsequent reduction at 923 K for 2 min and 10 min with 10 vol%  $CH_4$ , and another 10 min of 10 vol%  $CO_2$  reoxidation. Subsequently, for spectrum acquisition, the pre-treated samples were transferred to the XPS detection chamber without exposure to air. Data analysis was conducted using software (MultiPack 9.9.2; Ulvac-PHI). To account for surface charge effects, the energy of the spectrum was calibrated with the N1s peak (398.0 eV)<sup>21</sup>, derived from 3 wt% boron nitride (BN) mixed as an internal standard. Although C1s (approx. 248.8–

250.0 eV) is typically used for calibration, because of changes in C1s resulting from methane reactions, BN was used as a more suitable internal standard for this experiment.

*In situ* diffuse reflectance infrared Fourier transform spectrograms (*in situ* DRIFTS) of adsorbed CO were acquired using an FT-IR spectrophotometer (FT/IR-6200; Jasco Corp.) equipped with a ZnSe window and an MCT-M detector cooled with liquid nitrogen. Spectra were recorded with a resolution of 2 cm<sup>-1</sup>; 25 scans were averaged for each measurement. Before the measurements, for the fresh sample, the powder oxygen materials were pre-reduced by 20 vol% H<sub>2</sub> at 673 K for 30 min, followed by purging with Ar at 683 K for an additional 30 min. For reduced samples, CH<sub>4</sub> was introduced at 973 K for 5 min following pre-treatment. Regarding the oxidised samples, CO<sub>2</sub> was introduced for 10 min in the next step. Each spectrum was collected by averaging 64 scans with a resolution of 4 cm<sup>-1</sup> in the 4000–1000 cm<sup>-1</sup> range at 503 K. The experimental procedure involved the recording of the background and sample spectra. The samples were exposed to a mixture of 1 vol% CO-Ar at 503 K. The spectra were collected every 5 min. Upon saturation of adsorption, Ar was introduced into the cell. Then spectra were obtained every 0.5 min to monitor signal changes. The total flow rate was maintained as 50 mL min<sup>-1</sup>.

### **DRM-CL performance evaluation**

DRM-CL performance tests were investigated in a fixed bed quartz tube reactor (i.d. 8 mm) using 500 mg of the as-prepared oxygen carrier particles (355–500 μm) at atmospheric pressure. After the H<sub>2</sub> pre-reduction at 673 K for 30 min (H<sub>2</sub>: Ar = 1: 4; total flow rate: 50 mL min<sup>-1</sup>), the temperatures were changed to 773, 873, 923, 973, 1023, or 1073 K in Ar atmosphere for the following isothermal cycles of 1Ru/LCO. First, 10 vol% CH<sub>4</sub>/Ar was introduced into the reactor with a 50 mL min<sup>-1</sup> flow rate for 2 min in the reduction step. Subsequently, 10 vol% CO<sub>2</sub>/Ar was flowed into the tube with the flow rate of 50 mL min<sup>-1</sup> for 4 min in the reoxidation step for fully regenerating the oxygen carriers. Furthermore, a set of reduction and reoxidation steps was defined as one cycle of isothermal DRM-CL. The stability test for 1Ru/LCO was conducted by

repeating the cycle test 10 times at 923 K. It is noteworthy that the same first 2 min oxidation data were used for better comparison between the two steps even though CO<sub>2</sub> was flowed in for 4 min. Moreover, the same CH<sub>4</sub> and CO<sub>2</sub> flows were introduced for more than 8 min to obtain the kinetics profile of xRu/LCO. The products were detected and quantified using a quadrupole mass spectrometer (MS, BELMASS II; Microtrac Inc.). Before measurement, the mass detector was calibrated using various standard gases with known concentrations, all of which were similar to the reaction gas. To eliminate the secondary interference signal to CO caused by CO<sub>2</sub>, the CO concentration was obtained using the following equation, which removes the CO<sub>2</sub> fragments as

$$[CO]=S(m/z=28) - S(m/z=44) * f \quad (\text{eq. 9})$$

where  $f$  denotes the relation between the signals of  $m/z = 28$  and  $m/z = 44$ , which is determined by mass spectrometer measurements of different concentrations of constant CO<sub>2</sub> flow. The amount of a certain component is calculated by integrating the corresponding MS signals. The water generated in the reduction step was condensed by cold dehydration before entering the MS. The calculations of CH<sub>4</sub> conversion, CO selectivity, CO<sub>2</sub> conversion, H<sub>2</sub>/CO ratio, syngas yield, and CO yield are calculated as follows.

$$CH_4 \text{ conversion (\%)} = \frac{F \times \int_0^t ([CH_4]_{in} - [CH_4]_{out}) dt}{F \times \int_0^t [CH_4]_{in} dt} \times 100\% \quad (\text{eq. 10})$$

$$CO \text{ selectivity (\%)} = \frac{F \times \int_0^t [CO]_{out} dt}{F \times \int_0^t [CO]_{out} dt + F \times \int_0^t [CO_2]_{out} dt} \times 100\% \quad (\text{eq. 11})$$

$$H_2/CO = \frac{[H_2]_{out}}{[CO]_{out}} \quad (\text{eq. 12})$$

$$\text{Syngas yield} = \frac{F \times \int_0^t [CO]_{out} dt + F \times \int_0^t [H_2]_{out} dt}{22.4 \times m_{sample}} \quad (\text{eq. 13})$$

$$CO\ yield(POM) = \frac{F \times \int_0^t [CO]_{out} dt}{22.4 \times m_{sample}} \quad (\text{eq. 14})$$

Furthermore, carbon balance in the reduction step was inferred as

$$[CH_4]_{in} = [CH_4]_{out} + [CO_2]_{out} + [CO]_{out} + 0.5 * ([H_2]_{out} - 2*[CO]_{out}) \quad (\text{eq. 15})$$

CO<sub>2</sub> conversion during the reoxidation step is given as shown below.

$$CO_2\ conversion\ (\%) = \frac{F \times \int_0^t ([CO_2]_{in} - [CO_2]_{out}) dt}{F \times \int_0^t [CO_2]_{in} dt} \times 100\% \quad (\text{eq. 16})$$

The total CO yield during the reoxidation step is provided as presented below.

$$CO\ yield = \frac{F \times \int_0^t [CO]_{out} dt}{22.4 \times m_{sample}} \quad (\text{eq. 17})$$

In those equations,  $F$  represents the gas flow rate (mL min<sup>-1</sup>), [gas] stands for the corresponding gas concentration (%), and  $m$  signifies the mass of the sample (g).

The CO selectivity used in the study accounts for CO and CO<sub>2</sub> products, but it did not account for coke because the latter was subsequently converted into CO as well. The H<sub>2</sub>/CO ratio, which ideally should be equal to 2, is indicative of the carbon deposition in the reduction step.

A DRM-CL cycle stability test for the solid phase (oxygen carrier) was performed using a simultaneous thermal analysis apparatus (TGA; STA 2500 Regulus; Netzsch Inc.) with 30 mg of 1Ru/LCO material. After pre-reduction by 20 vol% H<sub>2</sub> (Ar balance; total flow rate: 50 mL min<sup>-1</sup>) at 673 K, the temperature was changed to 973 K in Ar atmosphere for the 10 successive isothermal cycles. The oxides were first reduced by 10 vol% CH<sub>4</sub> (Ar balance) for 10 min. Then they were re-oxidized with 10 vol% CO<sub>2</sub> for another 10 min. Furthermore, a set of a reduction and an oxidation step was defined as one cycle of isothermal DRM-CL. The total flow rate was set as constant: 100 mL min<sup>-1</sup>.

As calculated according to the following eq. 18, the amounts of reduction and oxidation (redox) were defined as the amounts of oxygen atoms released or restored in

each step. Considering the presence of carbon deposition, the actual reduction amounts are expected to be higher than the obtained results. Given the noticeable weight decrease in the TGA profile at the end of the reoxidation step, it is attributed to the burn-off of carbon. The weight of the consumed carbon is calculated using eq. 19.

$$\text{Reduction or Oxidation (Redox) amount [mmol g}^{-1}] = \frac{|\Delta m|}{m_{\text{sample}} \times M_{\text{O}}} \quad (\text{eq. 18})$$

$$\text{Consumed carbon weight [wt\%]} = \frac{|\Delta m_c|}{m_{\text{sample}}} * 100\% \quad (\text{eq. 19})$$

In those equations,  $\Delta m/\text{mg}$ ,  $\Delta m_c/\text{mg}$  (carbon weight in the oxidation step marked as green in Fig. 5A),  $m_{\text{sample}}/\text{g}$ , and  $M_{\text{O}}/\text{g mol}^{-1}$ , respectively represent the changes of sample weights during each step, the initial sample weight, and the molar mass of oxygen atom.

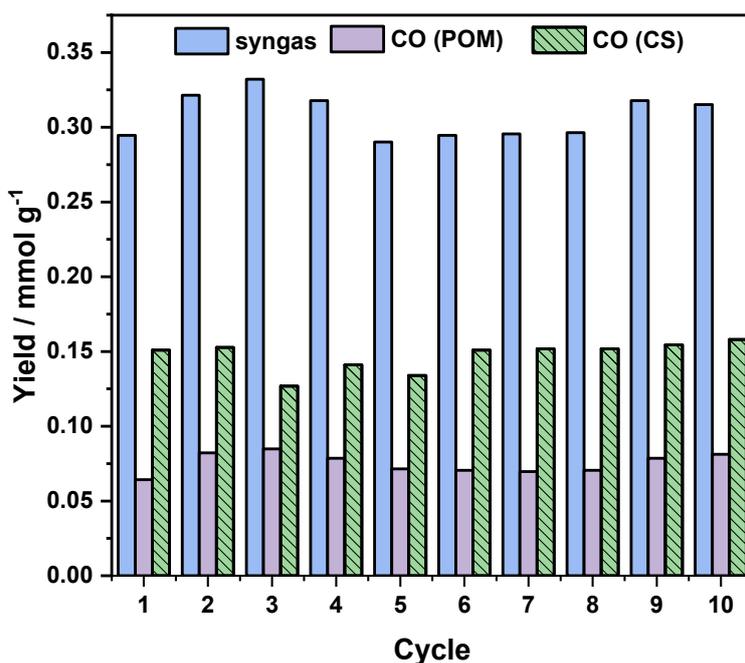


Fig. S2 Produced gas yield in both reduction step from POM reaction and oxidation step from CS reaction.

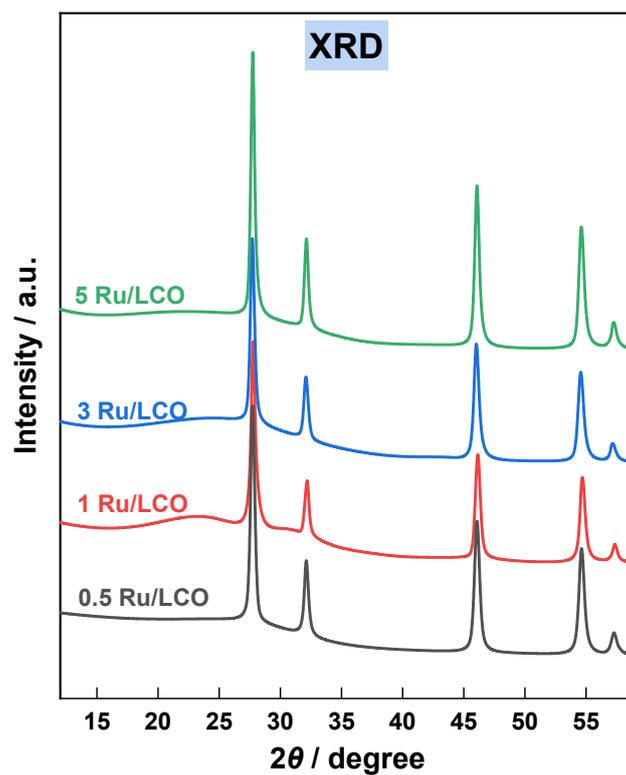


Fig. S3 XRD patterns of as made  $x$ Ru/LCO ( $x=0.5, 1, 3$  and  $5$ ) samples.

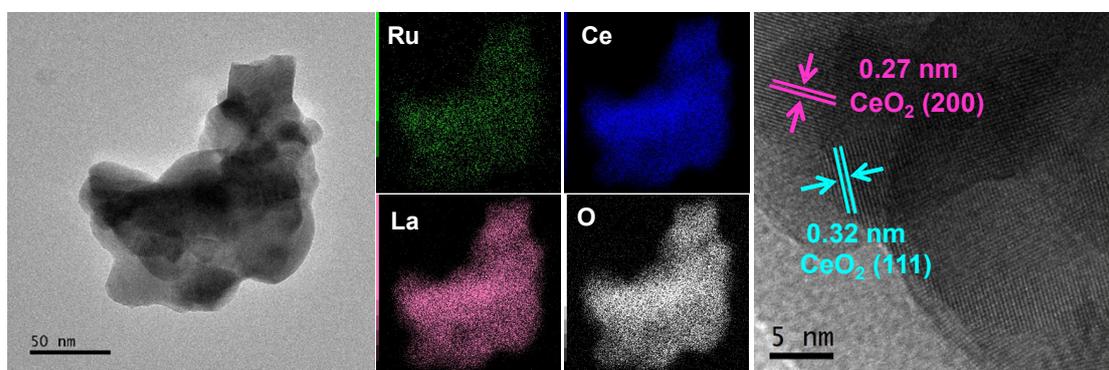


Fig. S4 STEM images, EDS element mappings and high-resolution STEM images over 10 cycled 1Ru/LCO sample.

Table S1 Textual parameters of the  $x$ Ru/LCO ( $x = 0, 0.5, 1, 3$  and  $5$ ) and  $\text{CeO}_2$ .

sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) <sup>a</sup>	Mean size (nm) <sup>b</sup>
$\text{CeO}_2$	/	64.9
LCO	/	20.8
0.5Ru/LCO	7.64	18.5
1Ru/LCO	7.86	20.7
3Ru/LCO	13.04	19.4
5Ru/LCO	7.56	21.6

<sup>a</sup> Determined by the BET method. <sup>b</sup> Estimated by the Scherrer equation based on the reflection of  $\text{CeO}_2$ .