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

The chemical looping method was applied to the reaction of methane and carbon dioxide, and the Ru/La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> catalyst + oxygen carrier showed high and stable activity for long cycles, even at low temperatures.

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

Keke Kang, Naoki Kayama, Takuma Higo, Clarence Sampson and Yasushi Sekine \*

Chemical looping dry reforming of CH<sub>4</sub>, a promising approach to reduce fossil fuel consumption and use CO<sub>2</sub>, hinges on designing an efficient oxygen carrier. However, high operating temperatures and unsatisfactory performance hamper its application. Loading a small amount of Ru promoter on the La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> oxygen carrier enhances CH<sub>4</sub> activation considerably, lowering the onset temperature to around 545 K. The Ru/La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> material exhibited impressive performance, achieving CH<sub>4</sub> conversion of around 65%, with almost negligible CO<sub>2</sub> produced during the reduction step and CO<sub>2</sub> conversion exceeding 95% during the CO<sub>2</sub> re-oxidation step over 10 redox cycles. Despite slight carbon deposition, the redox performance remains stable because of efficient carbon removal in the reoxidation step and the inherent structure stability of the oxygen carrier. This superior performance is attributed to the strong metal-support interaction between Ru and La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>, forming Ru–O–Ce bonds at the Ru<sup>δ+</sup>–CeO<sub>2-x</sub> interface. These bonds anchor active Ru onto stable La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> with excellent oxygen-ionic conductivity, enhancing CH<sub>4</sub> activation by increasing surface oxygen vacancies and maintaining structural stability with well-dispersed Ru promoters during cycles. Moreover, the migration of O<sup>2-</sup> in subsurface is promoted by creating an elevated oxygen chemical potential gradient induced by the oxygen-deprived surface, facilitated by the Ru promoter.

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## Introduction

Methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) are significant contributors to Earth's greenhouse effect. CH<sub>4</sub> resources are abundant and are readily accessible from the exploitation of shale gas or biogas. Therefore, converting CH<sub>4</sub> and CO<sub>2</sub> into other value-added chemicals, such as liquid fuels and hydrocarbons, has become a strategic focus worldwide.<sup>1,2</sup> Dry reforming of methane (DRM; eqn (1)), which simultaneously converts the main greenhouse gases of CH<sub>4</sub> and CO<sub>2</sub>, enables the production of a synthesis gas (syngas) of H<sub>2</sub> and CO. Diverse valuable chemical hydrocarbons, methanol, and acetic acid are producible *via* different processes using syngas.<sup>2</sup> Nevertheless, DRM entails challenges from high operation temperatures attributable to its endothermic nature. Additionally, it provides only diminished selectivity because of the side reaction of reverse water gas shift (RWGS; eqn (2)) and subsequent deactivation resulting from carbon deposition during CH<sub>4</sub> pyrolysis (eqn (3)) and the Boudouard reaction (eqn (4)).<sup>1,3</sup>



*Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, Japan.*

E-mail: [ysekine@waseda.jp](mailto:ysekine@waseda.jp)

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Catalytic chemical looping (CL) is a promising method for improving conventional DRM. As presented in Fig. 1, DRM-CL can be accomplished using metal oxides (MO<sub>x</sub>) acting as oxygen carriers, which gives out lattice oxygen continuously during the reduction step *via* partial oxidation of CH<sub>4</sub> reaction (POM; eqn (5)) and the lattice oxygen vacancy is refilled during the reoxidation step *via* CO<sub>2</sub> splitting reaction (CS; eqn (6)).

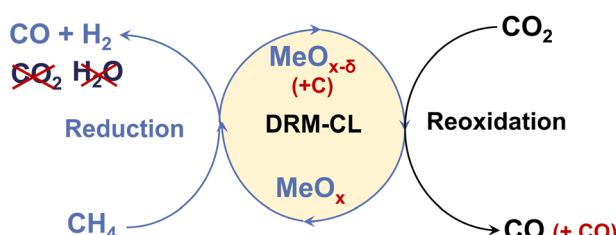
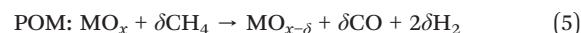


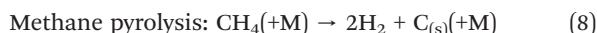
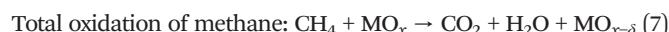
Fig. 1 Schematic image of DRM-CL process.





This process remains consistent with the catalytic DRM as a total, even though it involves two distinct gas–solid reactions. Although the overall process would still exhibit its inherent endothermic nature, using chemical looping presents several benefits that are not available when using conventional DRM. First, deactivation by carbon deposition is mitigated because the deposited carbon can be converted by  $\text{CO}_2$  via the reverse Boudouard reaction (eqn (4)), yielding additional CO during the oxidation step. Moreover, the RWGS side reaction is averted because the produced  $\text{H}_2$  is inherently separated from  $\text{CO}_2$ . Furthermore, the operational conditions can be individually optimised, leading to enhanced performance in specific instances because of the decoupling of reactions.

Selecting suitable oxygen carriers plays a crucially role in the DRM–CL process. However, this approach still presents several difficulties that must be addressed. First, syngas selectivity is diminished because of the presence of  $\text{CO}_2$  or  $\text{H}_2\text{O}$  resulting from the total oxidation of methane (eqn (7)). Second, earlier-reported oxygen carriers require high operating temperatures ( $>1073$  K), presenting an obstacle to their integration with downstream low-temperature processes such as Fischer–Tropsch (F–T) synthesis.<sup>4</sup> This limitation also hinders using various cost-effective industrial materials (e.g., stainless steel and so on) with lower melting points or recycled industrial waste heat.<sup>5</sup>



The primary hindrance to the reactivity in POM, particularly at lower temperatures, is the great amount of activation energy needed for lattice oxygen migration and removal. Furthermore, syngas selectivity is contingent on the type and abundance of surface oxygen species. Syngas selectivity is also influenced by the relative rates of bulk and subsurface oxygen conduction and surface oxygen reaction during the redox reactions. Moreover, the conduction of bulk and subsurface lattice oxygen to the oxide surface imposes limitations on the overall redox conversion.<sup>6–8</sup> Ce-based materials are highly appealing in DRM–CL because of their oxygen mobility and storage capacity.<sup>9–12</sup> From a thermodynamic perspective, the oxidation of reduced ceria by  $\text{CO}_2$  is favourable across a wide temperature range, from 298 K to over 1273 K.<sup>13</sup> Additionally, reduction from  $\text{CeO}_2$  to  $\text{Ce}_6\text{O}_{11}$  has been observed by Otsuka *et al.*<sup>14</sup> as occurring at temperatures as low as 923 K, which is consistent with thermodynamic calculations. Doping metals into  $\text{CeO}_2$  is an effective strategy for enhancing the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ .<sup>15,16</sup> Reportedly,  $\text{La}_2\text{Ce}_2\text{O}_7$  (denoted LCO) prepared by introducing lanthanum (La) into  $\text{CeO}_2$  can create a synergistic effect, leading to high stability and high oxygen-ionic conductivity.<sup>17–20</sup> Furthermore, Ru metal is selected as

the promoter because it is highly effective for methane activation, with high selectivity towards syngas, as reported in conventional DRM. It is also less expensive than other noble metals.<sup>21,22</sup> Therefore, we propose an investigation of the performance and properties of Ru/LCO as oxygen carriers for DRM–CL reaction.

As demonstrated by this study, loading small amounts of Ru (0.5 or 1 wt%) to LCO oxygen carrier can activate  $\text{CH}_4$  even at a low temperature of approximately 545 K. The 1 wt% Ru/ $\text{La}_2\text{Ce}_2\text{O}_7$  material exhibits remarkable performance, achieving  $\text{CH}_4$  conversion around 65%, with minimal  $\text{CO}_2$  produced during the reduction step and  $\text{CO}_2$  conversion exceeding 95% during the re-oxidation step at 923 K over 10 redox cycles. Despite a slight occurrence of carbon deposition during the reduction step, the redox performance remains stable over many cycles because of the efficient conversion of deposited carbon during the oxidation step and the inherent stability of the oxygen carriers. This improvement enables the broader application of DRM–CL, leading to considerable energy and cost savings. The exceptional performance is attributed to forming strong metal–support interaction (SMSI) between Ru and LCO, forming Ru–O–Ce bonds at the  $\text{Ru}^{\delta+}$ – $\text{CeO}_{2-x}$  interface. This interaction anchors active Ru components onto stable LCO with excellent ionic conductivity, enhancing methane activation by reducing the energy barrier through increased surface oxygen vacancies and maintaining structural stability with highly dispersed Ru promoters during many cycles. Moreover, the migration of  $\text{O}^{2-}$  in subsurface is promoted by creating an elevated oxygen chemical potential gradient induced by the oxygen-deprived surface facilitated by the Ru promoter.

## Results and discussion

### Screening of xRu/LCO catalysis–oxygen carrier

Fig. 2 shows the effect of the loading amount of Ru promoter on the redox performance of xRu/LCO as investigated using  $\text{CH}_4$ -TPR and isothermal redox experiments. Fig. 2A shows that only a small amount of Ru promoter can improve the  $\text{CH}_4$  activation ability of LCO efficiently, presenting lower  $\text{CH}_4$  activation onset temperatures at around 545 K. Furthermore, LCO exhibits a lower  $\text{CH}_4$  activation onset temperature of 731 K than that of  $\text{CeO}_2$ , with an almost

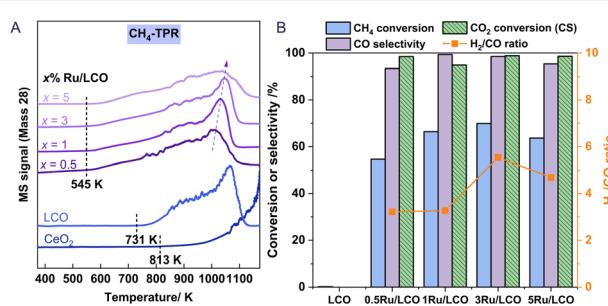


Fig. 2 (A)  $\text{CH}_4$ -TPR of xRu/LCO and  $\text{CeO}_2$ ; (B)  $\text{CH}_4$  conversion, CO selectivity during the reduction step and  $\text{CO}_2$  conversion during the reoxidation step of xRu/LCO at 923 K.

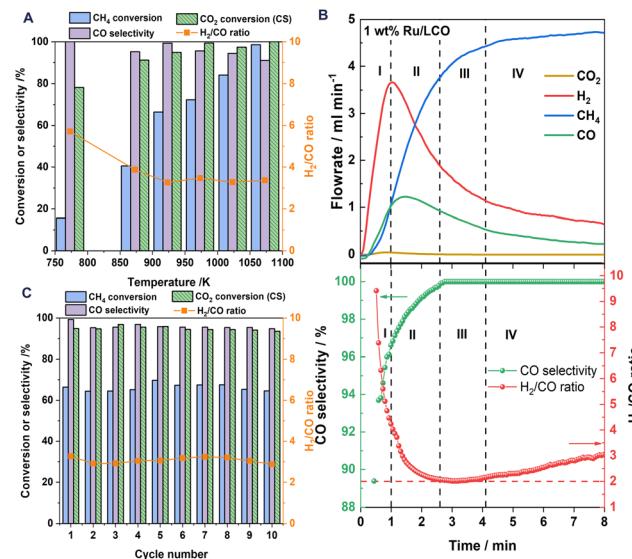


complete CO peak at around 1173 K, but no complete peak for  $\text{CeO}_2$  even at temperatures higher than 1273 K, which indicates that the doping of La improves the  $\text{CH}_4$  activation ability of  $\text{CeO}_2$ . Moreover, a lower loading amount of Ru promoter results in a lower temperature for the peak amount for CO production, indicating that low loading amounts as 0.5 or 1 wt% Ru promoter are able to activate  $\text{CH}_4$  toward syngas with superior performance. Therefore,  $x\text{Ru/LCO}$  exhibits promise for DRM-CL because of its capability to generate substantial oxygen vacancies at low temperatures (*ca.* 545 K) through reaction with  $\text{CH}_4$ .

Regarding performance during the reduction step at 923 K in Fig. 2B, all Ru-promoted samples exhibit CO selectivity exceeding 95% and  $\text{CH}_4$  conversion surpassing 50%. However, the performance results show that LCO remains almost inert for  $\text{CH}_4$  at 923 K without Ru promoter, highlighting the key role of Ru on  $\text{CH}_4$  activation. Most notably,  $\text{CH}_4$  conversion shows a volcanic shape with a maximum value of 70% when the loading amount is 3 wt%. The carbon deposition characterised by  $\text{H}_2/\text{CO}$  ratio also shows a volcanic shape with the most severe carbon deposition ( $\text{H}_2/\text{CO} = 5.5$ ) occurring when the loading amount is 3 wt%. A possible reason for these results is the following: When the loading amount of Ru promoter is less than 3 wt%, the  $\text{CH}_4$  activation is enhanced with the increased amount of Ru promoter. However, as shown in Table S1,<sup>†</sup> a loading amount of Ru promoter that is greater than 3 wt% leads to a larger mean particle size (obtained by XRD) and a smaller surface area (obtained by BET). Consequently, the active Ru promoters cannot be fully exposed to the oxygen carrier surface to activate  $\text{CH}_4$ . Regarding performance in the  $\text{CO}_2$  reoxidation step, nearly 100%  $\text{CO}_2$  conversion was achieved for all Ru-promoted samples. Above all, the findings indicate that satisfactory conversion and high selectivity can be attained at 923 K using very low-load Ru (0.5 or 1 wt%). Furthermore, considering the detection limit of characterisation instruments, 1Ru/LCO instead of 0.5Ru/LCO should be selected for additional study to obtain more precise surface characterisation results, although  $x = 0.5$  already shows satisfactory performance results at 923 K.

### Redox performance of 1Ru/LCO at different temperatures

Fig. 3A shows the redox performance of 1Ru/LCO during isothermal DRM-CL at various temperatures. 1Ru/LCO exhibits methane conversion of 16% at temperatures as low as 773 K, and it reaches almost 100% when temperatures rise to 1073 K. Regarding the carbon deposition characterised by  $\text{H}_2/\text{CO}$  ratio, it decreases as temperatures rise at temperatures lower than 923 K, but it reaches a stable value of approximately 3 at 923–1073 K. Although it is higher than the ideal value of 2, indicating the appearance of carbon deposition, it was verified later that all the carbon produced can be converted into additional CO *via* the reverse Boudouard reaction during the  $\text{CO}_2$  reoxidation step, resulting in zero net coke formation during DRM-CL.



**Fig. 3** (A) Comparison of the  $\text{CH}_4$  conversion, CO selectivity,  $\text{CO}_2$  conversion (CS reaction in the oxidation step) and  $\text{H}_2/\text{CO}$  ratio of 1Ru/LCO at different temperatures. (B) The evolved gas composition in the reduction step over 1Ru/LCO at 923 K: total methane oxidation region (region I), transition region (region II), partial methane oxidation region (region III); methane decomposition region (region IV). (C) Average  $\text{CH}_4$  conversion and CO selectivity as well as  $\text{H}_2/\text{CO}$  ratio in the reduction step and  $\text{CO}_2$  conversion in the oxidation step during 10 successive redox cycles over 1Ru/LCO at 923 K.

Furthermore, 1Ru/LCO shows CO selectivity higher than 90% within 773–1073 K, indicating a highly selective surface for the production of CO instead of  $\text{CO}_2$ . Moreover, excellent  $\text{CO}_2$  conversion of 78% at temperatures as low as 773 K and conversion approaching 100% over 973 K is obtained on 1Ru/LCO during the  $\text{CO}_2$  reoxidation step. Above all, based on a comprehensive consideration of the temperature, conversion rate and selectivity, a standard operation temperature of 923 K should be selected for the following isothermal redox performance evaluations.

### Kinetic profiles

Fig. 3B shows that profiles of  $\text{H}_2$  concentrations increase remarkably followed a little later by CO concentrations, with negligible  $\text{CO}_2$  produced when  $\text{CH}_4$  is introduced. According to the corresponding calculated  $\text{H}_2/\text{CO}$  ratio and CO selectivity, the reaction progress is divisible into four consecutive regions according to the  $\text{H}_2/\text{CO}$  ratio and CO selectivity. During the initial period (region I), the remaining active surface oxygen species after  $\text{H}_2$  pretreatment leads to total methane oxidation reaction and good catalytic performance of Ru metal for methane decomposition causing the carbon deposition. After gradual consumption of the surface oxygen species, the subsurface oxygen species can partially oxidise methane to CO and  $\text{H}_2$  (region III). A transition region (region II) is predominant between region I and region III. When oxygen species are consumed further, the region of carbon formation dominates by methane



decomposition (region IV). Therefore, the carbon deposition can be alleviated efficiently by controlling the reaction time of the reduction step with  $\text{CH}_4$ .

### Stability test

The long-term stability of 1Ru/LCO was studied by gas phase detection in the successive 10 redox cycles at 923 K, as portrayed in Fig. 3C. The 1Ru/LCO sample shows high  $\text{CH}_4$  conversion around 65% with almost no  $\text{CO}_2$  produced in the reduction step and  $\text{CO}_2$  conversion exceeding 95% for CS reaction in the reoxidation step at 923 K over 10 redox cycles. Although the  $\text{H}_2/\text{CO}$  ratio remains at around 3, the redox performance remains stable over cycles, demonstrating that the deposited carbon can be well converted during the oxidation step, indicating that the oxygen carrier is well regenerated, and showing that the structure remains stable over many cycles, as confirmed later from XRD and STEM findings. As shown in Fig. S2,† the CO yield in the CS reaction is twice that of the POM reaction. Therefore, the final  $\text{H}_2/\text{CO}$  ratio can be adjusted easily to different values as necessary using the CO produced in the reoxidation step.

To elucidate the state of carbon deposition during redox cycles, 10 redox cycle tests were also conducted using a thermal gravimetric analyser (TGA) by detecting the solid phase for visually observing the weight change caused by the change of carbon deposition. As presented in Fig. 4A, when flowing in  $\text{CH}_4$ , the weight of the oxygen carrier promptly decreases because of the migration of the lattice oxygen for the POM reaction. Then it increases slowly because of carbon deposition. Afterwards, when flowing in  $\text{CO}_2$ , it drastically increases to the maximum, first because of the refilling of lattice oxygen. Thereafter, it starts to decrease because of the consumption of the carbon deposited (marked in green) during the reoxidation step. The redox amount of lattice oxygen and the decrease carbon weight during each cycle are

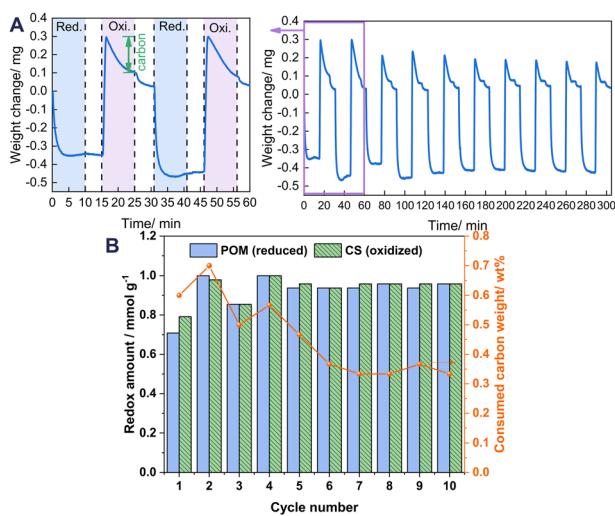


Fig. 4 (A) TGA of 1Ru/LCO during 10-cycle redox tests performed in alternating  $\text{CH}_4$  and  $\text{CO}_2$  flow. (B) Calculated data from the TGA profile.

calculated and presented in Fig. 4B. A large weight of consumed carbon and a higher oxidation amount than the reduction amount, were observed in cycle 1. After that, the consumed carbon weight during the oxidation step generally decreases along with the number of cycles before being stabilised from cycle 6, because 10 min oxidation by  $\text{CO}_2$  is insufficient to remove the high carbon amount completely from cycle 1, leading to carbon accumulation, which is removed with cycles and stabilised because of the lesser amounts of produced carbon during cycles after cycle 1. Accordingly, the redox amount stabilises from cycle 5 with the removal of accumulated carbon from the first cycles, indicating that good stability of 1Ru/LCO is obtainable even with a longer reaction time because of the successful removal of carbon by  $\text{CO}_2$ .

### Characterisations – structural and micromorphological evolution

Fig. 5A depicts the XRD patterns of the  $\text{CeO}_2$ , LCO, and 1Ru-promoted LCO samples: as-made, after reduction, after oxidation, and after 10 cycles. Only a simple pattern ascribed to the fluorite structure of  $\text{CeO}_2$  was observed, with no extra diffraction phases. This lack of extra diffraction phases illustrates that the fluorite structure of  $\text{CeO}_2$  is maintained after La substitution or Ru loading. The diffraction peaks of LCO shift towards lower degrees compared to those of  $\text{CeO}_2$ .

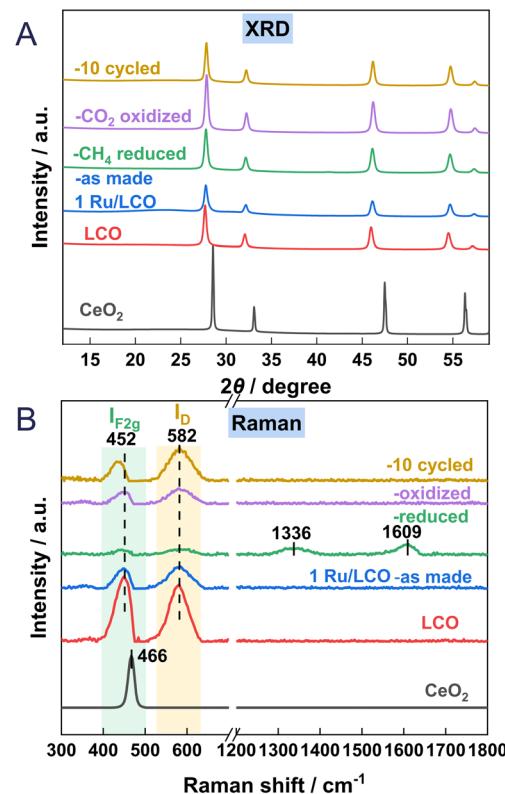


Fig. 5 (A) XRD patterns and (B) Raman profiles of  $\text{CeO}_2$ , LCO, 1Ru/LCO (as made, reduced, oxidised and 10 cycled) samples.



This shift results from the incorporation of  $\text{La}^{3+}$  into the lattice of  $\text{CeO}_2$ , leading to an increase in lattice parameters because of the augmented number of oxygen vacancies and the larger cation diameter of  $\text{La}^{3+}$ . The mean size of  $\text{CeO}_2$  is markedly smaller after La doping. There is no observable peak ascribable to Ru in  $x\text{Ru/LCO}$  in Fig. S3,† indicating that Ru is highly dispersed and that no phase separation occurs within 5 wt% loading amounts. It is noteworthy that no readily apparent shift or observable peak ascribable to Ru is observed between the diffraction peaks of the reduced, oxidised, and 10-cycled 1Ru/LCO samples, indicating that the 1Ru/LCO retains structural stability with Ru highly dispersed during 10 successive DRM-CL redox cycles. Moreover, as Table 1 shows, the mean size of 1Ru/LCO remained stable without remarkable change after reduction, oxidation, or even 10 cycles. This stability might be related to the formation of strong Ru-O-Ce bonds at the  $\text{Ru}^{\delta+}$ - $\text{CeO}_{2-x}$  interface, as confirmed by XPS results described hereinafter.

Raman spectroscopy was used to elucidate the oxygen vacancies formation in  $\text{CeO}_2$  lattice. Fig. 5B shows Raman spectra of  $\text{CeO}_2$ , LCO, 1Ru/LCO, and 1Ru/LCO during/after DRM-CL cycle samples. Strong peaks at approx.  $452\text{ cm}^{-1}$  attributed to the  $\text{F}_{2g}$  vibration mode of the Ce-O bond, are observed on all samples. Moreover, an additional peak at approx.  $582\text{ cm}^{-1}$  attributed to defect-induced (D) modes of the fluorite phase<sup>23,24</sup> was observed for samples related to LCO, indicating that the doping of La induces the appearance of the subsurface oxygen vacancies. Moreover, the ratios of  $I_D/I_{\text{F}_{2g}}$ , indicating the relative concentrations of oxygen vacancies in  $\text{CeO}_2$  lattice, are presented in Table 1. The higher  $I_D/I_{\text{F}_{2g}}$  ratio in 1Ru/LCO compared to that in LCO indicates that the introduction of a small amount of Ru promoter enhances the formation of oxygen vacancies effectively. This enhancement is likely to be attributable to the formation of a strong Ru-O-Ce bond at the  $\text{Ru}^{\delta+}$ - $\text{CeO}_{2-x}$  interface, as confirmed hereinafter based on XPS and *in situ* CO-DRIFTS results. The existing literature acknowledges that oxygen vacancies play a crucially important role in facilitating  $\text{CH}_4$  activation by reducing the dissociation barriers of  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  radicals.<sup>25</sup>

Moreover, the  $I_D/I_{\text{F}_{2g}}$  ratio of 1Ru/LCO greatly increases after reduction and decreases slightly after oxidation because the lattice oxygen was released in the reduction step and was refilled in the re-oxidation step. Two peaks at 1336 and 1609

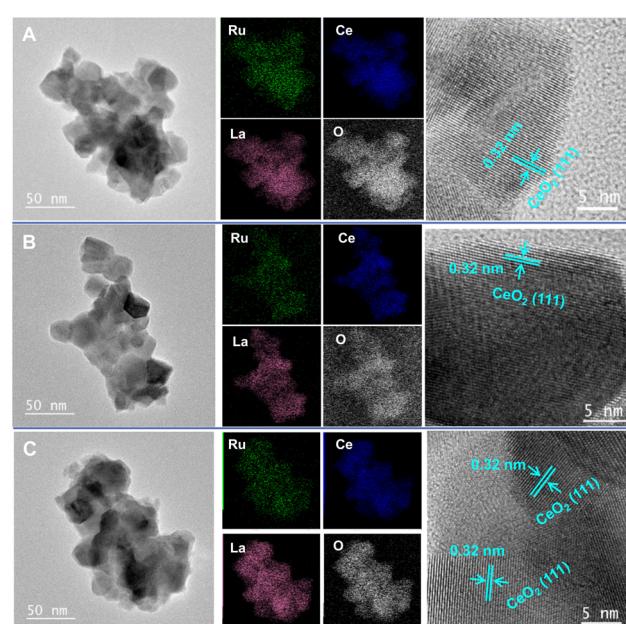
**Table 1** Textual parameters of the LCO and 1Ru/LCO as made and during DRM-CL

Sample	$S_{\text{BET}}^a$ ( $\text{m}^2\text{ g}^{-1}$ )	Mean size <sup>b</sup> (nm)	$I_D/I_{\text{F}_{2g}}^c$
LCO		20.8	0.88
1Ru/LCO-as made	11.2	20.7	1.10
1Ru/LCO-reduced	13.2	19.2	1.37
1Ru/LCO-oxidised	11.5	22.4	1.31
1Ru/LCO-10 cycled	7.3	23.8	1.67

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

$\text{cm}^{-1}$  attributed to carbon species were observed after reduction, but they disappeared during re-oxidation,<sup>26,27</sup> indicating that carbon deposited during the reduction step can be consumed by  $\text{CO}_2$  during the oxidation step. It is noteworthy that 1Ru/LCO shows a much higher the  $I_D/I_{\text{F}_{2g}}$  ratio than after first oxidation after 10 cycles because more lattice oxygen is involved with reduction by  $\text{CH}_4$  for 10 times.

The STEM, EDS element mappings, and high-resolution STEM results obtained for the fresh, reduced, and oxidised 1Ru/LCO are depicted in Fig. 6, whereas those for the 10 cycled 1Ru/LCO are presented in Fig. S4,† The STEM images revealed that the particle size of 1Ru/LCO remains consistent at 20–30 nm throughout the entire DRM-CL process, even after 10 cycles (consistent with mean size results calculated from XRD in Table 1), further confirming the structural stability of 1Ru/LCO. However, the CO pulse experiment revealed a mean diameter of Ru metal at 265.6 nm, which deviates considerably from results obtained using STEM and XRD. This disparity can be attributed to the formation of surface  $\text{Ru}^{\delta+}$  resulting from SMSI effects between Ru and  $\text{La}_2\text{Ce}_2\text{O}_7$ . This formation decreases the amount of CO adsorption on the surface Ru metal and engenders inaccurate results for the Ru particle size. This observation indirectly underscores the presence of SMSI in the system. Moreover, high-resolution STEM images show that only two lattice fringes corresponding to (111) and (200) of  $\text{CeO}_2$  are detected in the samples of fresh, reduced, oxidised, and 10 cycled 1Ru/LCO.<sup>28,29</sup> This single-phase of  $\text{CeO}_2$  with the apparent absence of La and Ru particles suggests that La particles are well incorporated into the crystalline phase of  $\text{CeO}_2$ , whereas Ru components exist as highly dispersed  $\text{RuO}_x$  species over the LCO, aligning with XRD results. Of paramount



**Fig. 6** STEM images, EDS element mappings and high-resolution STEM images of 1Ru/LCO (A) fresh, (B)  $\text{CH}_4$  reduced, (C)  $\text{CO}_2$  re-oxidised samples.



importance is that the results of EDS element mappings demonstrate that all elements, especially Ru, maintain high dispersion throughout the entire DRM-CL process, even after 10 cycles. No aggregation is observed, reflecting that Ru particles are anchored on the stable LCO support through the strong Ru-O-Ce bond at the  $\text{Ru}^{\delta+}-\text{CeO}_{2-x}$  interface, ensuring high stability.

### Surface chemistry

As illustrated in Fig. 7A, the XPS Ce 3d spectra exhibit five pairs of  $3d_{5/2}$  and  $3d_{3/2}$  characteristic peaks. Three pairs, with peaks at 881.7, 887.9, and 897.2 eV, each accompanied by peaks at 900.1, 906.6, and 916.8 eV, are attributed to  $\text{Ce}^{4+}$  species, whereas the remaining two pairs are associated with  $\text{Ce}^{3+}$  species (some peaks with nearly zero area values appear as a result of fitting optimisation).<sup>30,31</sup> The  $\text{Ce}^{3+}$  ratio, calculated using the peak areas of  $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ , is an important indicator of the oxygen vacancies on ceria surfaces.<sup>32,33</sup> It is noteworthy that the  $\text{Ce}^{3+}$  ratio of the samples after  $\text{CH}_4$  reduction at 923 K is markedly lower than that of the fresh sample, pretreated with  $\text{H}_2$  at 673 K for 30 min. This finding is likely attributable to the heating process from 673 K to 923 K,

which accelerates the diffusion of oxide ions inside the oxygen carrier material. Consequently, the oxygen vacancies become more homogeneously distributed in the surface and subsurface layers, potentially resulting in a relative reduction in the surface  $\text{Ce}^{3+}$  ratio. Moreover, the  $\text{Ce}^{3+}$  ratio increases consistently from 9.6% to 13.3% with  $\text{CH}_4$  reduction from 2 min to 10 min, indicating augmentation in oxygen vacancies on ceria surfaces resulting from the POM reaction through the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . Subsequently, the  $\text{Ce}^{3+}$  ratio decreases markedly to 3.6% after 10 min of  $\text{CO}_2$  reoxidation, indicating the efficient refilling of surface oxygen vacancies through the oxidation of  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$ .

In the XPS spectra of C 1s + Ru 3d (Fig. 7B), the Ru 3d<sub>5/2</sub> is commonly used to understand the charge state of Ru species because of the overlapping of Ru 3d<sub>3/2</sub> and C 1s peak at approximately the 284.8 eV position. Throughout the entire redox process, peaks attributed to partially charged Ru nano particles ( $\text{Ru}^{\delta+}$ ) at around 280.8 eV position are observed. This phenomenon is associated with charge transfer during the formation of the Ru-O-Ce species, contributing to the enhancement of oxygen vacancies. Similar observations have been reported widely for other ceria-supported Ru systems. Liu *et al.*<sup>10</sup> reported that the Ru nanoparticles supported on ceria with  $\text{Ru}^{\delta+}$  and O decoration exhibit much better stability than those with only metallic  $\text{Ru}^0$  under steady-state DRM conditions because of their sustained active chemistry. Furthermore, earlier theoretical investigations into the activation of methane over  $\text{CeO}_2$ -supported transition metals suggested that strong interaction between the metal and ceria support and acquisition of positive charges constitute markedly lower methane activation barriers.<sup>25,34,35</sup>

Simultaneously, the spectra and quantitative results presented in Table 2 reveal continuous accumulation of surface carbon (approx. 284.9 eV) attributable to methane decomposition during the reduction by  $\text{CH}_4$  from 2 to 10 min. This carbon accumulation decreases considerably to levels lower than those after 2 min of  $\text{CH}_4$  reduction following 10 min of  $\text{CO}_2$  reoxidation. This decrease further confirms the consumption of deposited carbon during  $\text{CO}_2$  reoxidation, which is consistent with results obtained from Raman and TGA analyses.

To gain additional insights into the surface adsorption condition changes occurring during the DRM-CL process of 1Ru/LCO, *in situ* CO-adsorption DRIFTS was performed for the fresh, reduced, and oxidised 1Ru/LCO. The results are presented in Fig. 8. Upon the fresh 1Ru/LCO surface in Fig. 8A, IR bands at 2176 and 2116  $\text{cm}^{-1}$ , attributed to

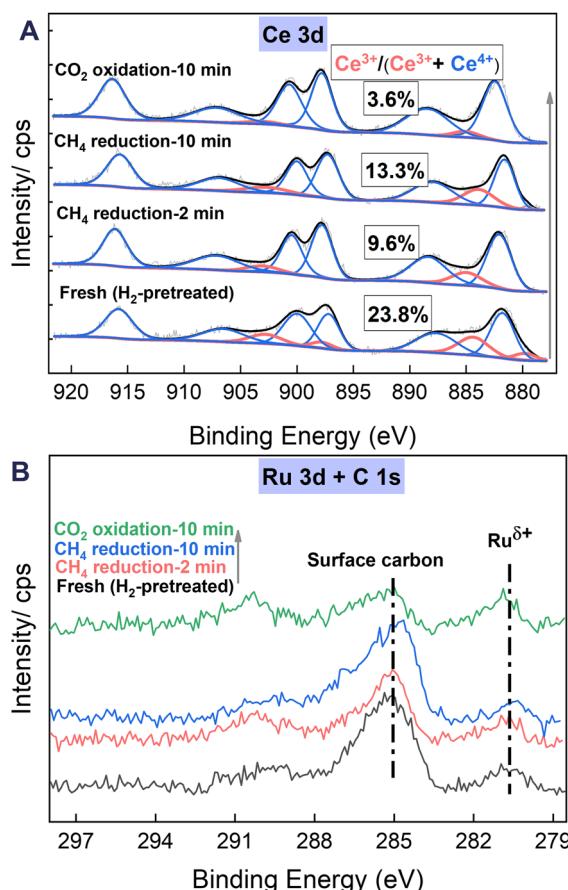


Fig. 7 The XPS data for the (A) Ce 3d and (B) C 1s + Ru 3d regions of the 1Ru/LCO sample after undergoing a series of sequential pretreatments:  $\text{H}_2$  pretreatment at 673 K for 30 min,  $\text{CH}_4$  reduction at 923 K for 2 and 10 min, and  $\text{CO}_2$  reoxidation at 923 K for 10 min.

Table 2 Quantitative results of XPS for the 1Ru/LCO sample after undergoing a series of sequential pretreatments

Sample	Ce	La	O/atom%	C	Ru
$\text{H}_2$ treatment	9.7	13.0	53.7	23.4	0.2
$\text{CH}_4$ 2 min	10.5	14.0	57.2	18.1	0.2
$\text{CH}_4$ 10 min	9.8	12.8	53.8	23.5	0.1
$\text{CO}_2$ 10 min	10.8	14.8	61.3	12.9	0.2



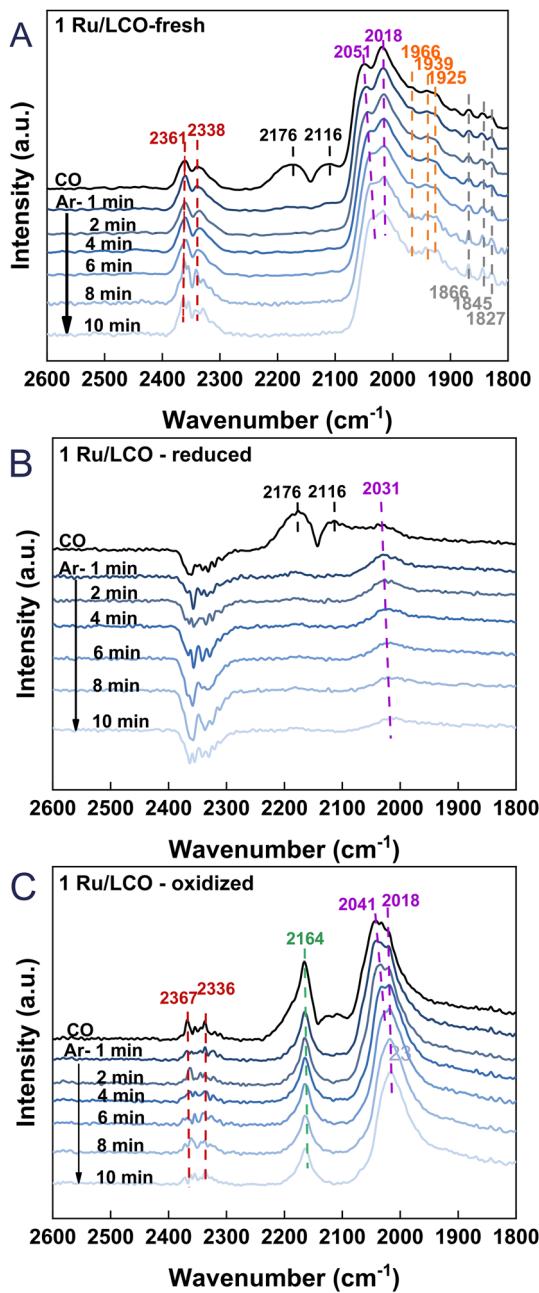


Fig. 8 *In situ* CO-DRIFTS of 1Ru/LCO (A) fresh (B) reduced by  $\text{CH}_4$  and (C) oxidized by  $\text{CO}_2$ .

gaseous CO, disappear rapidly after 1 min Ar purging. Additionally, bands at 1866, 1845, and 1827  $\text{cm}^{-1}$  correlated with bridge-bound CO adsorption on Ru atoms are observed along with two prominent bands at 2051 and 2018  $\text{cm}^{-1}$  assigned to linearly absorbed CO on Ru atoms,<sup>36–38</sup> showing that Ru species are well-dispersed on the surface. It is noteworthy that bands are visible at 1966, 1939, and 1925  $\text{cm}^{-1}$ , corresponding to CO adsorption on the interface of the Ru metal and LCO support.<sup>39,40</sup> These further validate the XPS results, indicating interactions between the LCO support and Ru clusters. On the reduced 1Ru/LCO surface in Fig. 8B, except for the quickly disappearing bands attributed to

gaseous CO, only one band associated with absorbed CO on Ru atoms remains, resulting from the surface partially covered by carbon deposited from  $\text{CH}_4$  decomposition. On the oxidised sample surface in Fig. 8C, bands related to Ru metal atoms reappear, suggesting that  $\text{CO}_2$  reoxidation removes deposited carbon effectively, thereby uncovering the surface and regenerating the adsorption sites of the material for the next cycle. Additionally, a distinctive band is apparent at 2164  $\text{cm}^{-1}$ , attributed to CO adsorbed onto  $\text{Ce}^{4+}$  cations with different unsaturated coordination.<sup>41–43</sup> That band constitutes evidence for the completion of oxygen vacancy refilling and oxygen migration from the subsurface to the surface during the transition from  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$ . Importantly, IR bands at 2361 and 2338  $\text{cm}^{-1}$  positions, attributed to linearly or physically adsorbed  $\text{CO}_2$ ,<sup>26,44</sup> resulting from the reaction between CO adsorbed onto surface oxygen vacancies and oxygen species, were observed on both fresh and oxidised sample surfaces. Those bands reflect an abundance of surface oxygen vacancies for  $\text{CH}_4$  activation, related to the strong interaction through the formation of Ru–O–Ce. This interaction endures even after cycling, demonstrating the remarkable stability of 1Ru/LCO.

## Discussion

Based on analyses of structural and electronic properties, the proposed reaction processes of DRM-CL over 1Ru/LCO oxygen carrier are presented in Fig. 9. Specifically, in the reduction step, the activated  $\text{CH}_4$  releases the lattice oxygen through the transition from  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , with the formation of oxygen vacancies. Then in the oxidation step,  $\text{CO}_2$  is adsorbed and dissociated on the surface of 1Ru/LCO oxygen carrier with progress of the oxidation step, thereby re-filling the oxygen vacancies. This sequence is repeated iteratively, completing each redox cycle. The presence of surface Ru<sup>δ+</sup> plays a crucially important role in enhancing the performance of both the oxidation and reduction steps and contributing to the overall cyclic stability.

The  $\text{CH}_4$ -TPR and redox performance presented in Fig. 2 and 3 demonstrate the remarkable efficiency of a small amount of 0.5 or 1 wt% Ru promoter for enhancing the  $\text{CH}_4$  activation ability of LCO. This enhancement leads to a low  $\text{CH}_4$  activation onset temperature of approximately 545 K, achieving approximately 65%  $\text{CH}_4$  conversion, even at 723 K. Raman (Fig. 5B), XPS (Fig. 7), and *in situ* CO-adsorption

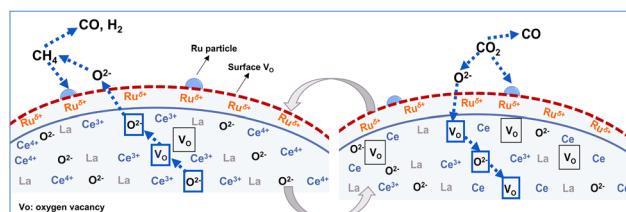


Fig. 9 Proposed reaction processes of DRM-CL over 1Ru/LCO oxygen carrier.

DRIFTS (Fig. 8) results emphasise the fundamentally important role played by oxygen vacancies and the Ru–O–Ce bond formed because of SMSI in supporting the superior CH<sub>4</sub> reactivity. The formation of Ru–O–Ce bonds at the RuO<sub>x</sub>–CeO<sub>2–x</sub> interface, as supported by density functional theory calculations<sup>45</sup> and experiments,<sup>46</sup> decreases the oxygen vacancy formation energy, consequently improving low-temperature CH<sub>4</sub> reactivity. Moreover, the well-dispersed Ru<sup>δ+</sup> species in the form of Ru–O–Ce bonds contribute to mobile and active oxygen ions for DRM–CL processes.

The performance results presented in Fig. 3 also show CO<sub>2</sub> conversion greater than 95% at 723 K in the CO<sub>2</sub> reoxidation step. Earlier studies of surface-promoted oxygen carriers highlight the importance of the potential gradient between the oxide bulk (or subsurface) and surface induced by the prompted surface for O<sup>2–</sup> migration.<sup>8</sup> In our case, the oxygen-deprived surface in the presence of Ru establishes an increased oxygen chemical potential gradient between the oxide subsurface and surface. This enhancement engenders improved O<sup>2–</sup> migration, facilitated by the redox reaction between Ce<sup>3+</sup> and Ce<sup>4+</sup> in the subsurface of the oxygen carrier, ultimately completing the chemical looping process and promoting CO<sub>2</sub> conversion.

Cycle stability tests for the gas phase demonstrate excellent redox performance over 10 cycles (Fig. 3C and 4A), with observation of the removal of the deposited carbon in the reoxidation step by TGA (Fig. 4), Raman (Fig. 5B and Table 1), and XPS (Fig. 6 and Table 2). Additionally, XRD (Fig. 6A), BET (Table 1), and STEM-EDS (Fig. 6) findings demonstrate that the structure of 1Ru/LCO remains stable after 10 cycles, with Ru maintaining a highly dispersed state. This state is attributed to the formation of Ru–O–Ce bonds anchoring active Ru onto stable La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> with excellent ionic conductivity, highlighting its strong anti-aggregation capability.

## Conclusions

Ru/La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> catalytic chemical looping material is highly effective for enhancing CH<sub>4</sub> activation even at low temperatures (545 K). The 1 wt% Ru/LCO demonstrates remarkable performance, achieving CH<sub>4</sub> conversion of approximately 65%, with minimal CO<sub>2</sub> production during the reduction step and CO<sub>2</sub> conversion exceeding 95% during the CO<sub>2</sub> re-oxidation step at 923 K over 10 redox cycles. Despite encountering slight carbon deposition during the reduction step, the redox performance maintains stability in 10 successive cycles because of the efficient carbon conversion which occurs during the reoxidation step and because of the inherent structure stability of the oxygen carrier. This exceptional performance is attributed to the establishment of a strong metal–support interaction between Ru and La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>, forming crucially important Ru–O–Ce bonds. These bonds anchor the active Ru species onto the stable and ionic conductive La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> substrate. This mechanism enhances CH<sub>4</sub> activation by increasing surface oxygen vacancies. Moreover, it maintains

structural stability with well-dispersed Ru promoters throughout the cyclic process. Furthermore, the oxygen-deprived surface induced by Ru presence creates an elevated oxygen chemical potential gradient between the oxide subsurface and surface, improving O<sup>2–</sup> migration for the redox reaction between Ce<sup>3+</sup> and Ce<sup>4+</sup> in the subsurface of the oxygen carrier to accomplish the chemical looping process effectively.

## Author contributions

Conceptualisation: KK and YS, funding acquisition: YS, investigation: KK, NK, CS, project administration: YS, supervision: YS, validation: KK, NK, TH, CS, YS, visualization: KK, writing – original draft: KK, writing – review & editing: YS.

## Conflicts of interest

There are no conflicts to declare.

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