# Journal of Materials Chemistry A



View Article Online

View Journal | View Issue

# PAPER

Check for updates

Cite this: J. Mater. Chem. A, 2019, 7, 27347

Received 17th June 2019 Accepted 1st November 2019

DOI: 10.1039/c9ta06471k

rsc.li/materials-a

### 1. Introduction

Direct production of synthesis gas  $(CO/H_2)$  *via* solar energydriven thermochemical splitting of carbon dioxide and water is a promising renewable energy source for fuel consuming sectors. However, extensive research is required to develop methods to dissociate  $CO_2$  and  $H_2O$  into CO and  $H_2$  at temperatures less than 2000 K for sustainable and economical renewable fuels. In addition, gas separation problems at such high temperatures are an ever existing challenge.<sup>1,2</sup> Thermochemical splitting of  $CO_2$  (CDS) and  $H_2O$  (WS) *via* two step reduction–oxidation (redox) cycles mediated by active metal oxides as oxygen carriers has been extensively studied and proven to be highly effective in mitigating the above mentioned challenges whilst achieving large scale production of synthesis gas.<sup>3,4</sup> The quantity of cyclic reduction–oxidation of oxygen

## Enhanced oxygen exchange capacity in nanostructured vanadia-ceria multi-phase oxygen carriers for solar thermal fuel production<sup>†</sup>

Asim Riaz,<sup>a</sup> Muhammad Umair Ali, <sup>b</sup> Wojciech Lipiński <sup>b</sup>\*<sup>a</sup> and Adrian Lowe \*<sup>a</sup>

Developing an efficient redox material is a fundamental and crucial step in sustainable hydrocarbon fuel production via solar energy-driven thermochemical redox cycles. Vanadium being the 20th most abundant element in the earth's crust, with excellent catalytic properties combined with other oxide materials can potentially be a suitable candidate for efficient solar fuel production. Here, we report a first demonstration of a facile strategy to effectively utilize vanadium oxide with ceria for thermochemical H<sub>2</sub>O and CO<sub>2</sub> splitting with superior oxygen exchange capacity and efficient H<sub>2</sub> and CO yields of 68% more than the pure nano-structured ceria. We observe a synergic effect in oxygen exchange capacity and ion mobility in the vanadia-ceria binary phase system, where vanadia provides more reducing states for the hydrocarbon oxidation, while ceria acts as an oxygen buffer for the re-oxidation of reduced vanadia. We demonstrate that the addition of a carbon dioxide step between the methane partial oxidation and H<sub>2</sub>O splitting step activates the oxygen carrier by creating sufficient oxygen vacancies for the controlled oxidation of methane and avoiding methane cracking for over 100 cycles. The extraordinarily high oxygen exchange capacity observed in 25% V–CeO<sub>2</sub> resulted in superior and pure H<sub>2</sub> yields of 220 mL  $g^{-1}$  during the water splitting step of sequential water and carbon dioxide splitting, while maintaining a H<sub>2</sub>/CO ratio close to 2. Finally, these findings suggest that the facile combination of the extraordinary catalytic properties of vanadia and superior oxygen ion mobility of ceria can be a powerful approach for an efficient and effective solar thermochemical fuel production.

carriers is a key factor in determining the fuel yield, which directly depends upon the operating temperature and atmosphere. Inert gas sweeping  $(IGS)^{2.5-10}$  and methane partial oxidation  $(MPO)^{1,11-17}$  are the most commonly studied metal oxide reduction methods, where MPO promotes the reduction of metal oxide at temperatures as low as 1073 K when compared to the operating temperature of IGS, *i.e.*, T > 1673 K.<sup>9,12,18,19</sup> This MPO-driven metal oxide reduction ensures high solar-to-fuel efficiencies of up to 54%, compared to 19% in IGS cycles.<sup>11,19,20</sup> Consequently, synthesis gas can be produced at an industrial scale with adjustable H<sub>2</sub>-to-CO ratios required for gas-to-liquid fuel conversion by a Fischer–Tropsch (FT) process.<sup>21</sup>

High oxygen exchange capacity with fast fuel production rates and high cyclability under harsh operation conditions are challenging to achieve. Ceria has emerged as a highly attractive redox material choice for thermochemical syngas production due to its fast kinetics and fuel selectivity.<sup>1,3,22-24</sup> However, ceria possesses low oxygen exchange capacities (below 0.25 mol<sub>O</sub>/ mol<sub>Ce</sub>) and is highly dependent on the geometrical structure including surface area, pore size and particle size for efficient oxygen ion mobility.<sup>1,3,25-30</sup> Ceria supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO *etc.* has reportedly improved its initial oxygen exchange capacity with structural and morphological stability over several cycles at

<sup>&</sup>lt;sup>a</sup>Research School of Electrical, Energy and Materials Engineering, The Australian National University, Canberra, ACT 2601, Australia. E-mail: wojciech.lipinski@anu. edu.au; adrian.lowe@anu.edu.au; Tel: +61 2 612 57896; +61 2 612 54881

<sup>&</sup>lt;sup>b</sup>Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ta06471k

temperatures as high as 1273 K.<sup>31</sup> On the other hand, doping ceria with transition metals (Mn, Cu, Zr, Fe *etc.*) results in stable reaction rates due to enhanced surface and bulk oxygen mobility and reactivity.<sup>14,15,32–36</sup> However, doped ceria has lower reaction kinetics than pure ceria, which results in overall low fuel production performance.<sup>33</sup>

The catalytic nature of vanadia has been utilized for depollution reactions via selective oxidation of hydrocarbons.37,38 Kodama et al. reported V2O5 as an oxygen carrier, yielding 25.9% CO, 5.1% CO2 and 83.5% and 16.5% selectivity for CO and H<sub>2</sub> respectively, during MPO at 1173 K.39 Vanadiasupported structures on SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and CeO<sub>2</sub> have extensively been studied for hydrocarbon oxidation.<sup>37,38,40-42</sup> A combination of the high oxygen ion mobility of CeO<sub>2</sub> and the high reduction extent of surface vanadia species near the ceria makes the Ce-V-O system an attractive candidate for hydrocarbon oxidation. In addition, vanadia-ceria stabilizes the surface Ce<sup>3+</sup> sites by moderating the valence change ability of the  $Ce^{3+}/Ce^{4+}$  pair with cyclic formation of  $CeVO_4/CeVO_3$  in the redox activity.41 Thus, the study of Ce-V-O systems is vital for high temperature reforming of methane for solar fuel production with high and stable reaction rates.

Here, we report a method for stabilizing the reaction rates and structural parameters of ceria by utilizing the vanadia-ceria binary phase system, synthesized by a facile liquid phase precursor combustion method. Compared to the conventional impregnation method, liquid phase precursor combustion methods deliver better control of particle size, morphology and dispersion of vanadia particles on the ceria. Structural studies of Ce-V-O systems revealed that surface vanadia species on ceria play an important role in achieving stable reaction rates over 100 cycles during H<sub>2</sub>O and CO<sub>2</sub> splitting at 1173 K. Oxidation of Ce-V-O during CDS, WS, WS-CDS and WS-CDS after MPO also reveals interesting facts about metal-CO2 and metal-H<sub>2</sub>O interactions. We observed that sequential WS and CDS cycles enhanced the hydrogen purity and production yield during the WS step. In addition, higher and more stable MPO rates were achieved when compared to pure nano-structured ceria. We also observed that the combination of vanadia and ceria greatly stabilized the microstructure and specific surface area of pure nano-structured ceria. We believe that this study may be useful in the development of new, efficient oxygen carriers for upscale production of solar fuel via thermochemical redox reactions. Specifically, the sequential WS and CDS cycling can be utilized on the wide range of oxygen carriers reported earlier, e.g., recently developed Ce-doped Mn<sub>3</sub>O<sub>4</sub> (ref. 43) and La-doped strontium manganates.10

### 2. Experimental

#### 2.1. Materials preparation

Ultra-fine, nano-structured CeO<sub>2</sub> and *x*VCeO<sub>2</sub> (x = 0%: CeO<sub>2</sub>, 25%: CV25, 50%: CV50, 75%: CV75, 100%: V<sub>2</sub>O<sub>5</sub>) nanoparticles were synthesized by a facile liquid phase precursor decomposition method.<sup>44</sup> The synthesis method offered upscale production of nanoparticles with good control on the particle size and morphology. Briefly, the precursor solution for CeO<sub>2</sub> was

prepared by dissolving cerium(m) nitrate hexahydrate (CeN<sub>3</sub>O<sub>9</sub>· $6H_2O$ , Aldrich) in ethanol and stirred until complete dissolution. For the precursor solution of *x*VCeO<sub>2</sub>, separate solutions of stoichiometric concentration of vanadium(v) oxytripropoxide (C<sub>9</sub>H<sub>21</sub>O<sub>4</sub>V, Aldrich) and CeN<sub>3</sub>O<sub>9</sub>· $6H_2O$  in ethanol were mixed and stirred at room temperature until complete homogeneous solutions were achieved. The precursor solutions were dried at 353 K and then fired at 1173 K for 2 h. The ramp rate for drying and firing was kept constant at 3 K min<sup>-1</sup>. The synthesis schematic for these oxygen carriers is shown in Fig. 1a.

#### 2.2. Thermochemical cycling

The cycling thermochemical redox performance of pure nanostructured ceria and CV25 was evaluated in a vertical-tube reactor placed inside an infrared gold image furnace (P4C-VHT, Advance Riko).  $250 \pm 5$  mg powder samples were placed between 2  $\pm$  0.3 mm thick layers of highly porous and temperature resistant alumina-based fibrous wool (AlBF-1, 97% Al<sub>2</sub>O<sub>3</sub> and 3% SiO<sub>2</sub>, ZIRCAR). The samples and wool layers were centrally located in the alumina tube to ensure uniform heating, as shown in Fig. 1b. Powder mass was recorded before and after cycling to monitor the weight loss at the appropriate part of the process. A weight loss of 15  $\pm$  2 mg was observed after cycling which may be due to cycle chemistry and possible leftover powder on the inner walls of the alumina tube. Lower material activity was observed for sample masses greater than 300 mg because the small diameter of the alumina tube limits the mass transfer in solid-gas reactions during redox cycling. Gas flow rates are regulated with flow rate controllers (F201CV, Bronkhorst), operated using an in-house developed LabVIEW (National Instrumental<sup>TM</sup>) program code which is integrated with mass flow controllers and pneumatically actuated valves (1315R, Swagelok). The sample temperature was monitored using a B-type thermocouple sealed in an alumina sheath, located directly under the packed samples. The composition of the product gases was recorded using a quadrupole mass spectrometer (OmniStar™ GSD 320, Pfeiffer Vacuum).

The tubular reactor was purged with argon (Ar grade 5.0) with a flow rate of 500 mL min<sup>-1</sup> before every reduction and oxidation reaction, to remove any surface gas species (H<sub>2</sub>, CO and CO<sub>2</sub>) from the sample/tube/fitting surfaces, which may potentially affect the product gas composition. The reactor was heated in an inert atmosphere (Ar, 500 mL min<sup>-1</sup>) from ambient temperature to an optimized isothermal operating temperature of 1173 K at a ramp of 100 K min<sup>-1</sup>. The powder samples were reduced in a gas flow of 20 mL min<sup>-1</sup> CH<sub>4</sub> (grade 4.5), diluted with 230 mL min<sup>-1</sup> Ar flow.  $CO_2$  splitting by reduced metal oxide samples was carried out in the presence of 4% vol of CO<sub>2</sub> (grade 4.5) with a flow of 10 mL min<sup>-1</sup> diluted with a 240 mL min<sup>-1</sup> Ar flow. For water splitting, steam vapor was generated at 368 K in a bubbler filled with DI water. An Ar flow of 30 mL min<sup>-1</sup> passed through the bubbler to carry the steam vapors and was further diluted by an Ar flow of 220 mL min<sup>-1</sup> before delivering the vapors into the reactor tube. The total gas flow during the reduction and oxidation step was kept constant at 250 mL min<sup>-1</sup>.



**Fig. 1** Schematic illustration of the synthesis procedure: (a) flow diagram of the synthesis of vanadia–ceria mixed-metal oxide nano-powders. (b) Schematic diagram indicating the tubular reactor set-up utilized for performing redox cycle experiments, mass-spectrometer used to analyze the reactant and product gases and the temperature program control.

Inert gas sweeping was done with argon at a flow rate of 500 mL min<sup>-1</sup> before and after each reduction and oxidation step and repeated for each cycle. The sequence and duration of the gas flow during CO<sub>2</sub> and H<sub>2</sub>O cycles was Ar (5 min)/CH<sub>4</sub> (20 min)/Ar (5 min)/CO<sub>2</sub> or H<sub>2</sub>O (10 min). In the case of coupled H<sub>2</sub>O and CO<sub>2</sub> splitting cycles the sequence for MPO–WS–CDS was Ar (5 min)/CH<sub>4</sub> (20 min)/Ar (5 min)/H<sub>2</sub>O (7 min)/Ar (5 min)/CO<sub>2</sub> (7 min) and for MPO–CDS–WS the gas flow sequence was Ar (5 min)/CH<sub>4</sub> (20 min)/Ar (5 min)/CO<sub>2</sub> (7 min)/Ar (5 min)/H<sub>2</sub>O (7 min). The redox performance of nano-powders was tested over 10 preliminary cycles, followed by a stability test over 100 cycles. Changes in the structure and chemical nature of the oxide samples were studied after the 1st reduction, 10 cycles and 100 cycles during the CO<sub>2</sub> and H<sub>2</sub>O splitting phase.

#### 2.3. Materials characterization

Powder samples were characterized before and after the thermochemical cycles. X-ray diffraction (XRD) analysis was carried out using a D2 phaser diffractometer (Bruker). The samples were scanned using a Cu K $\alpha$  (1.54 Å) radiation source with an operating voltage of 30 kV and a current of 10 mA. XRD patterns were recorded with a scanning rate of 0.75° min<sup>-1</sup> in a 2 $\theta$  range of 10–80° at an increment of 0.02°. Crystalline domain size was determined by applying the Scherrer equation on the most intense peaks obtained in the XRD patterns. Phase quantification was carried out by the Rietveld refinement technique utilizing Match 3 V. 3.8.1.143 (Crystal Impact) software.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer (XPS) microprobe equipped with a 180° double focusing hemispherical analyzer. A monochromatic Al K-Alpha source with a spot size of 200–900  $\mu$ m was operated at a power of 180 W (15 kV × 12 mA). The total pressure in the chamber was maintained at around 10<sup>-8</sup> mbar. Two different spots on a 5 × 5 mm area of sample with an estimated depth of 4 mm were scanned with an energy of 160 eV. The pass energy was reduced to 40 eV for high resolution spectra. The data processing was performed using CasaXPS processing software version 2.3.18 (Casa Software Ltd, Teignmouth, UK). The aliphatic carbon peak C 1s at 284.8 eV was used as a reference for the binding energies of elements acquired in the survey spectra.

Structural analysis of the redox materials was carried out by utilizing a Raman imaging microscope (Renishaw Plc, model 2000) coupled with an Olympus BH2 microscope. The microscope is equipped with a motorized XYZ stage, air-cooled CCD detector and a CCD camera. The samples were excited by using a 785 nm NIR laser source and spectra were recorded in a Raman shift range of 100–1200 cm<sup>-1</sup>. The samples were exposed for 20 s with an accumulation of 3 and the power was adjusted from 0.01% to 0.5% (<6 MW) according to the sample response.

A field emission scanning electron microscope (FESEM, Zeiss Ultraplus) was utilized to observe the morphology of nanostructured powders before and after thermochemical redox cycles. Particle size distribution and lattice plane spacing were determined using a high-resolution transmission electron microscope (HR-TEM, JEOL 2100F) with an operating voltage of 200 kV. The samples were deposited onto lacey carbon-coated 200 mesh copper grids. Primary particle size and lattice plane spacing were acquired *via* the ImageJ image processing software. Energy dispersive X-ray spectroscopy mapping (EDX) was performed *via* the scanning transmission electron microscopy (STEM) mode on a JEOL 2100F, to acquire information about the chemical composition of 25% VCeO<sub>2</sub> (CV25) before and after MPO–WS–CDS cycles. The area of interest was scanned using the STEM probe to obtain elemental mapping and EDX spectra.

Information about the specific surface area and porosity of nano-structured powder samples was acquired  $via N_2$  adsorption-desorption isotherms at 7 K by utilizing a TriStar II,

Micromeritics. Powders were degassed at 523 K under vacuum (0.1 mBar) for 3 h prior to the measurements.

## 3. Results

A structural comparison of as-prepared pure nano-structured ceria and CV25 nanoparticles is shown in Fig. 2a and b, representing a similar nanoscale morphology consisting of agglomerated semi-spherical particles with an average diameter of 15  $\pm$ 



**Fig. 2** Chemical and morphological characterization of pure nano-ceria and CV25: HRTEM images representing the size and morphology of asprepared (a) pure ceria and (b) CV25, nanoparticles. Inset in (b) shows *d*-spacings of vanadium and cerium present in CV25. EDS spectra of (c) asprepared and (d) reduced CV25 nanoparticles. STEM EDS (e) grey scan and (f) overlay mapping of reduced CV25 showing the distribution of Ce (green), V (blue) and C (red) in samples after methane partial oxidation.

#### Paper

3 nm. High-resolution transmission electron microscopy (HRTEM) analysis of samples reveals similar semi-spherical nanoparticles exposing two distinct lattice spacings of 0.437 nm and 0.307 nm corresponding to the (010) and (111) planes of vanadia and ceria, respectively (Fig. 2b). These findings confirm the two distinct phases of ceria and cerium vanadate, observed in the XRD patterns with crystallite sizes of 12 nm and 13 nm for pure nano-structured ceria and CV25 respectively.

Energy dispersive X-ray spectroscopy (EDX) analysis reveals distinct emission energy peaks of Ce, V and carbon content before and after methane partial oxidation of CV25, as shown in Fig. 2b and c. The SRTEM EDS mapping of the reduced CV25 sample represents the elemental distribution of vanadium, cerium and carbon after the methane partial oxidation reaction, as shown in Fig. 2e and f. The intensity of the carbon peak is higher in the reduced CV25 sample than in the as-prepared CV25 sample, which indicates possible carbon deposition on the metal oxide.

XRD patterns of as-prepared nanoparticles are presented in Fig. 3a. Pure ceria consists of a dominant peak of the triclinic crystal structure with a low-angle shoulder of cubic CeO<sub>2</sub>. Asprepared nano-structured ceria is calcined at 600 °C and 900 °C to further investigate this behavior. Low temperature calcination resulted in amorphous-like triclinic structures (*i.e.* very small grain sizes) while at the higher calcination temperature, a more defined crystalline triclinic ceria is seen with shoulder peaks of cubic ceria. A comparison of XRD patterns obtained from calcined, commercial, reference triclinic and cubic ceria structures is presented in Fig. S1 in the ESI.† Addition of vanadium results in an increase in the CeVO<sub>4</sub> phase with V concentrations greater than 25%, where high vanadium contents promote the conversion of CeO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> into CeVO<sub>4</sub> *via* the following solid state reaction.<sup>40</sup>

$$V_2O_5 + 2CeO_2 \rightarrow 2CeVO_4 + \frac{1}{2}O_2$$
 (1)

Evolution of the CeVO<sub>4</sub> phase can be observed from the growth of shoulder peaks at  $2\theta = 48.2^{\circ}$  and doublets at  $2\theta =$ 32.87° with the increase in V greater than 25%. Controlled conversion of CeO2 and V2O5 into CeVO4 was observed up to 25% V loading, where a mixture of CeO<sub>2</sub> and CeVO<sub>4</sub> with a ratio of  $CeO_2$ :  $CeVO_4$  (~3) is achieved. However, a further increase in vanadium concentration results in a drastic decline in the CeO<sub>2</sub> concentration by 96% with 75% V addition. This can be visualized by the ratio of  $CeO_2$  to  $CeVO_4$  intensities ( $I_{CeO_2}/I_{CeVO_4}$ ) evaluated from XRD patterns of as-prepared vanadia-ceria systems, presented in Fig. S2.<sup>†</sup> Large quantities of V<sub>2</sub>O<sub>3</sub> up to 46.1% are also observed along with only 17% CeVO<sub>4</sub> with 75% V addition. Thus, a V-Ce-O system with 25% vanadia loading is investigated as a suitable candidate material to study the combined effect of CeO2 and CeVO4 phases for solar fuel production performance evaluation.

Methane partial oxidation promotes the conversion of  $V^{5+}$  to V<sup>3+</sup> at high temperatures due to the leaching of oxygen from CeVO<sub>4</sub>, resulting in additional peaks of the CeVO<sub>3</sub> phase in CV25, as shown in Fig. 3b. Lower CeO<sub>2</sub> content is also observed in reduced CV25, which is evident from the decline in the CeO<sub>2</sub> peak intensity near 33°. After 10 consecutive MPO-CDS and MPO-WS-CDS cycles, oxygen recovery is highest resulting in up to 65% of CeO2 and 25% CeVO4. However, CV25 after MPO-WS and MPO-CDS-WS redox cycles contains a significant amount of CeVO<sub>3</sub> phase up to 23.7%, which indicates an incomplete oxidation of CeVO<sub>3</sub> to CeVO<sub>4</sub>. This phenomenon can be related to the carbon deposition on oxygen carriers which hinders the re-oxidation of reduced species, resulting in few oxygen species in the material being available for an efficient methane reforming reaction. Consequently, it results in further methane cracking with high H<sub>2</sub> products and low CO emission, resulting in a high H<sub>2</sub>/CO ratio. This is evident from the syngas production rates and yields of MPO-WS cycles. However, addition of a CDS step after WS oxidizes carbon from the surface of the oxygen carrier which reduces methane cracking during the MPO step. This can easily be verified by comparing the H<sub>2</sub>/CO ratios



Fig. 3 Structural analysis of vanadia–ceria multi-phase systems before and after redox cycles: (a) XRD patterns representing the structural evolution in pure nano-ceria with the addition of vanadium  $xVCeO_2$  (x = 0%, 25\%, 50\%, 75\% and 100\%) with discrete phases of CeO<sub>2</sub>, CeVO<sub>4</sub>,  $V_2O_5$  and CeVO<sub>3</sub>. (b) Phase analysis of CV25 before and after thermochemical redox cycling highlighting the reduction and oxidation behaviour of CeO<sub>2</sub> and CeVO<sub>4</sub> during fuel production.

of CV25 during MPO-WS, MPO-WS-CDS and MPO-CDS-WS. High fuel production yields during MPO-CDS and MPO-WS-CDS cycles with high fuel selectivity are achieved when compared to that of the MPO-WS and MPO-CDS-WS cycles, which will be explained later.

The surface of the CV25 and ceria samples was further investigated by X-ray photoelectron spectroscopy (XPS), as presented in Fig. 4. The oxidation states of cerium and vanadium ions were determined from the XPS spectra. The presence of tetravalent cerium ions can be confirmed from the Ce 3d peaks observed in the pure nano-structured ceria and CV25 samples, as shown in Fig. 4a. The Ce 3d 3/2, 5/2 peaks are shifted towards higher binding energies with addition of V, *i.e.* CV25, which corresponds to the presence of a 3+ oxidation state in the cerium.<sup>45</sup> The intensity of the dominant peak at ~917.0 eV associated with the Ce<sup>4+</sup> ions increases after reduction of CV25 indicating the formation of CeVO<sub>3</sub>, (Fig. 4c). The Ce<sup>4+</sup> peak at ~917 eV in the CV25 sample after MPO–WS cycling is more intense as compared to that of the MPO–CDS and MPO–CDS– WS cycles, indicating high CeVO<sub>3</sub> contents, which supports the XRD findings. The intense O 1s peak at 529.7 eV is observed due to the presence of surface oxygen species (Fig. 4b). Two peaks associated with V  $2p_{3/2}$  and V  $2p_{1/2}$  in pure V<sub>2</sub>O<sub>5</sub> and CV25 samples were observed at ~517.2 eV and ~524.1 eV, respectively. These peak positions correspond to the V<sup>5+</sup> oxidation state of vanadium.<sup>46</sup> A shift in the V  $2P_{3/2}$  peak towards low binding energy is observed in CV25 samples after reduction and all other redox cycles (Fig. 4d). This shift corresponds to the presence of V<sup>3+</sup> species along with V<sup>5+</sup> due to the co-existence of CeVO<sub>4</sub> and CeVO<sub>3</sub> phases, as discussed in the XRD section.

XPS data are utilized to quantify the atomic% of Ce, V and oxygen in terms of Ce/V and V/O ratios, as shown in Table 1. The Ce/V ratio showed a decline of 3–5% in the CV25 sample after the redox cycles, indicating the loss of vanadium due to possible volatilization of vanadium at high temperatures.<sup>47</sup> Segregation of CeO<sub>2</sub> and CeVO<sub>4</sub> phases may also be a reason for a nonhomogeneous vanadium distribution, resulting in less vanadium in the area scanned using the XPS probes. No significant



**Fig. 4** Surface analysis of vanadia–ceria mixed-metal oxides: (a) XPS spectra representing the  $Ce^{4+}/Ce^{3+}$  oxidation state in pure nano-ceria and CV25; (b) XPS spectra representing the V<sup>5+</sup> oxidation state and surface oxygen in pure vanadia and CV25. XPS spectra of the CV25 sample after MPO, MPO–CDS, MPO–WS, MPO–WS–CDS and MPO–CDS–WS redox cycles representing change in (c) Ce 3d and (d) V 2P signature peaks.

Table 1 Elemental quantification (atomic %) of surface vanadium, cerium and oxygen species in CV25 samples before and after redox cycles. The elemental data are obtained from XPS analysis and quantified including Ce, V, O and C

	Elemer concen	ntal tration (%	Elemental ratios		
Sample ID	V	Ce	0	V/O	Ce/V
CeO <sub>2</sub>	_	30	55	_	_
$V_2O_5$	35.24		47.26		0.75
CV25	20.02	12.5	46.67	0.43	0.62
Reduced CV25	19.11	12.42	44.22	0.43	0.65
CV25 after MPO-CDS	18.3	7.28	41.13	0.44	0.4
CV25 after MPO-WS	16.66	9.22	34.98	0.48	0.55
CV25 after MPO-WS-CDS	16.07	9.23	41.81	0.38	0.57
CV25 after MPO-CDS-WS	13.57	9.29	35.76	0.38	0.68

change in the overall values of V/O ratios is observed because both vanadium and oxygen species show a decline on the CV25 surface after cycling. However, the depletion of surface oxygen species is higher in CV25 after MPO–WS and MPO–CDS–WS when compared to that of the MPO–CDS and MPO–WS–CSD redox cycles. The Ce/V ratio is also subjected to a decrease in Ce and V species after redox cycles. The lower content of cerium suggests that vanadium-containing phases dominate the CV25 surface reactions during redox cycles when compared to ceria.

The nature of the interactions between ceria and vanadia is further investigated from the information obtained by Raman spectroscopy, as shown in Fig. 5. Pure nano-structured ceria and CV25 were analyzed before and after redox cycles, as shown in Fig. 5a and b, respectively. A Raman spectrum of as-prepared pure vanadia nanoparticles was used as a reference. The presence of ceria phase in pure ceria and CV25 is confirmed by the band at 464.88 cm<sup>-1</sup>, corresponding to the  $F_{2g}$  symmetry of the cubic structure. The Raman bands at 279.14 and 711.14 cm<sup>-1</sup> validate the formation of crystalline V<sub>2</sub>O<sub>5</sub> nanoparticles along with the surface vanadia species (V=O) at 122.25 and 970– 1030 cm<sup>-1</sup>, in pure nano-vanadia samples.<sup>48,49</sup> Two Raman bands related to the V–O–Ce and V–O–V bridging modes of CeVO<sub>4</sub> at 787.84 cm<sup>-1</sup> and 799.21 cm<sup>-1</sup>, along with the bands at 861.25, 379.54 and 259.19 cm<sup>-1</sup> confirm the formation of CeVO<sub>4</sub>. The disappearance of the V=O band at 970–1030 cm<sup>-1</sup> and a decline in the intensity of the CeO<sub>2</sub> band at 461.87 cm<sup>-1</sup> are also related to the conversion of CeO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> into CeVO<sub>4</sub> by the solid–state reaction (eqn (1)).

A decrease in the ratios of the signature peaks of CeVO<sub>4</sub> at  $861 \text{ cm}^{-1}$  to CeO<sub>2</sub> at  $461 \text{ cm}^{-1}$  is observed after the redox cycles, which indicates a decrease in CeVO<sub>4</sub> concentration and formation of CeVO<sub>3</sub>. This ratio in CV25 is lowest after MPO–WS and highest after MPO–CDS cycling. The XPS findings on possible vanadium loss and oxygen depletion in CV25 samples after MPO–WS and MPO–CDS–WS redox samples can be verified by the decline in the signature peak of the V=O species at 122.25 cm<sup>-1</sup>. In contrast, this peak is most intense after reduction and MPO–CDS, followed by MPO–WS–CDS redox cycling, indicating high concentrations of available surface vanadia species for methane partial oxidation reaction. This finding supports the better reforming performance during MPO–CDS and MPO–CDS–WS redox cycling as compared to that of MPO–WS and MPO–CDS–WS redox cycling.

Oxygen exchange capacity and redox rates of pure nanostructured ceria and CV25 were evaluated *via* 10 consecutive two-step thermochemical redox cycles. The reduction and oxidation behaviors and performance in terms of fuel production rates and yields were evaluated during MPO–CDS, MPO– WS, MPO–WS–CDS and MPO–CDS–WS redox cycling. Methane conversion was calculated using eqn (E1) (ESI†), to investigate the material's behavior during the methane partial oxidation reaction. Table T1 (ESI†) shows the methane conversion by pure ceria and CV25 samples during the MPO–CDS, MPO–WS, MPO– WS–CDS and MPO–CDS–WS redox cycle tests performed in this study. CV25 clearly shows a higher methane conversion when compared to that of pure ceria in all four-cycle tests. Comparing the methane conversion seen in the four types of cycle tests, it is highest during MPO–CDS followed by the MPO–WS–CDS redox



Fig. 5 Structural characterization of oxygen carriers: (a) Raman spectra of as-prepared pure nano-ceria, pure vanadia and CV25 nanoparticles, representing the presence of fingerprint peaks of  $CeO_2$ ,  $V_2O_5$  and  $CeVO_4$ ; (b) Raman spectra of CV25 nanoparticles as-prepared and after MPO, MPO–CDS, MPO–WS, MPO–WS–CDS and MPO–CDS–WS redox cycles.

cycles and lowest in the MPO–WS cycles, indicating inferior methane reforming during MPO–WS cycling.

High rates of syngas production during the reduction step of MPO-CDS by CV25 are observed with an average rate of 12.96 mL min<sup>-1</sup> g<sup>-1</sup> and 4.88 mL min<sup>-1</sup> g<sup>-1</sup> for H<sub>2</sub> and CO respectively, Fig. 6a and c. The calculated H<sub>2</sub>/CO ratio was close to 2 with an average value of around 2.15, indicating controlled methane partial oxidation (Table T2<sup>†</sup>). In contrast, the average production rates for H<sub>2</sub> and CO produced by pure nano-structured ceria were only 7.12 mL min<sup>-1</sup> g<sup>-1</sup> and 2.47 mL min<sup>-1</sup> g<sup>-1</sup>, respectively. However, methane cracking is observed after the first cycle of the MPO-WS process, resulting in significant increases in the H<sub>2</sub>/CO ratio reaching up to a value of around 4.59 and 3.38 in pure nanostructured ceria and CV25 respectively. Moreover, the water splitting rate was close to 10 mL min<sup>-1</sup> g<sup>-1</sup> – more than double that of the pure nano-ceria *ca.* 4.25 mL min<sup>-1</sup> g<sup>-1</sup>, as shown in Fig. S3a and S3c.<sup>†</sup> The CO selectivity S(CO) was determined from the cycle data, by utilizing eqn (E2) in the ESI.<sup>†</sup> A higher value of S(CO) is obtained for CV25 during the MPO-WS-CDS cycles when compared to that of pure nano-structured ceria. Elevated production rates of CO<sub>2</sub> in the MPO step of MPO-WS cycling

result in lower CO selectivity. Carbon deposition on the oxygen carriers can be associated with this, which may possibly promote methane cracking instead of reforming of methane, resulting in high  $\rm H_2/\rm CO$  ratios being obtained during MPO–WS cycling.

Reaction kinetics play a critical role in the  $H_2$  and CO redox rate profiles, which are greatly affected by the amount of reactant gasses reaching the oxygen carrier. In a fixed bed reactor design, the homogeneous concentration of reactant gases reaching the oxygen carriers is limited by the gas flow through solid materials, which greatly influences the  $CH_4$ -to- $O_2$  ratios. It is observed that in the beginning of the MPO reaction, small amounts of  $CO_2$  are produced due to low  $CH_4$  concentrations, as shown in real time gas profiles obtained from the mass spectrometer (Fig. S4†). As the required concentration of  $CH_4$  is achieved and stabilized, no  $CO_2$  is observed, and reaction rates of  $H_2$  and CO are increased.

Sequential WS and CDS reaction tests after the MPO step were performed to investigate the oxidation behavior of these nano-structured oxygen carriers in  $CO_2$  and  $H_2O$  as oxidizing media (Fig. 6b and d). In the first attempt, WS–CDS cycles were performed after the MPO reduction of oxygen carriers, while



Fig. 6 Thermochemical redox cycle performance evolution in terms of production rates of H<sub>2</sub>, CO and CO<sub>2</sub> during MPO–CDS and MPO–WS–CDS cycles on: (a) and (b) pure nano-structured ceria; (c) and (d) CV25.

#### Paper

flushing with Ar for 5 min at 500 mL min<sup>-1</sup> before each oxidation step. The reduction rate profile for both the oxygen carriers changed after the first cycle, where an increase in the H<sub>2</sub> production rate was observed after 4 min of reduction and reached its maximum value after the maximum rate of CO was achieved. A significant improvement in the H<sub>2</sub>/CO ratio is achieved in the MPO step of the MPO-WS-CDS redox cycle when compared to simple MPO-WS cycles. The highest calculated H<sub>2</sub>/CO ratio from CV25 was 3.1 at the 5th cycle, subsequently decreasing and becoming stable at around 2.21. However, in the case of pure nano-structured ceria, the ratio appeared to be unstable and fluctuated from 3.4 to 2.8. The H<sub>2</sub> production rates of pure nano-structured ceria were observed to be unstable during the WS step of the MPO-WS-CDS cycles, despite achieving rates as high as 10.21 mL min<sup>-1</sup> g<sup>-1</sup> for a few cycles. In contrast, CV25 exhibited high and stable rates of water splitting reactions up to 15.12 mL min<sup>-1</sup> g<sup>-1</sup>, with considerable stability throughout the 10 cycles. This finding indicates possible structural stability in pure nano-structured ceria induced by the surface vanadia particles, which additionally improve the ion mobility in the structure.

The counter effect of steam on methane reforming is studied by performing MPO-CDS-WS cycling (Fig. S3b and S3d<sup>†</sup>). After the first cycle, the H<sub>2</sub> production rate increased significantly with a H<sub>2</sub>/CO ratio reaching 6.3 and 4.8 for pure nanostructured ceria and CV25, respectively. The CO production rate during the MPO step did not undergo a substantial increase for CV25 and a considerable amount of CO<sub>2</sub> was observed. However, deterioration in the CO production rates was observed in pure nano-structured ceria. The presence of H<sub>2</sub> in the CDS oxidation step indicates the presence of residual methane in the system. It is worth noting that the H<sub>2</sub> during the second oxidation (*i.e.* WS), clearly reveals the presence of oxygen vacancies in the structure of the oxygen carriers due to an incomplete re-oxidation during the CDS cycle. Moreover, the presence of a small amount of CO2 also indicates the possible carbon deposition on the surface of the oxygen carriers during MPO and CDS reactions.

The total fuel production data along with information about  $H_2/CO$  ratios and CO selectivity S(CO), recorded during the

whole duration of each reduction and oxidation step of every cycle is presented in Tables T2 and T3.<sup>†</sup> Evidently, CV25 produced nearly double the yield of H<sub>2</sub> and CO when compared to pure nano-structured ceria, with a near ideal H<sub>2</sub>/CO ratio of 2.12 and CO selectivity up to 90.14%, during MPO-CDS redox cycles. Despite the high H<sub>2</sub> (78.2 mL g<sup>-1</sup>) and CO (19.9 mL g<sup>-1</sup>) yields produced by pure ceria, the H<sub>2</sub> yield during oxidation is still lower than that produced by CV25. This is possible because of less oxygen vacancies produced during the methane partial oxidation step of the MPO-WS redox cycles, which results in low H<sub>2</sub> yields in the H<sub>2</sub>O splitting reaction.

Introducing a CDS step after the WS reaction improves the overall methane reforming process and lowers the  $H_2/CO$  ratio. In addition, the  $H_2$  yield during the WS step is higher and more stable in MPO-WS-CDS cycling than in the simple MPO-WS redox cycles. However, utilizing WS as a complementary step for CDS in MPO-CDS-WS cycling exhibits inefficient reduction of oxygen carriers in the MPO step, as observed in the MPO-WS cycles. A considerable amount of  $H_2$  up to 3.4 mL g<sup>-1</sup> is produced by CV25 in the WS step along with a small amount of  $CO_2$  (around 1.1 mL g<sup>-1</sup>). However, a drop in the CO yield during the MPO and CDS step of the MPO-CDS-WS cycle is observed in pure nano-structured ceria when compared to the simple MPO-CDS.

The average total CO yield calculated for pure nano-structured ceria and CV25 during the reduction and oxidation reactions is shown in Fig. 7. Methane partial oxidation by CV25 resulted in H<sub>2</sub> and CO yields of up to 130.12 mL  $g^{-1}$  and 87.34 mL  $g^{-1}$ , respectively, which is more than double of that produced by pure ceria during MPO-CDS redox cycles. A decline in CO yields by 300% in CV25 and 170% in pure ceria was observed after the addition of the WS step after CDS during MPO-CDS-WS cycling. The H<sub>2</sub> products showed a considerable increase, suggesting an inefficient reforming of methane. Similar to rate-based information, yields of H<sub>2</sub> produced during the methane partial oxidation showed a drastic increase during MPO-WS redox cycles. Addition of the CDS step after the WS step, i.e. MPO-WS-CDS, not only improved the H<sub>2</sub>/CO ratio but also increased the H<sub>2</sub> yields resulting from splitting of H<sub>2</sub>O. The reasons for this phenomenon have been discussed in previous sections.



Fig. 7 Thermochemical redox cycle performance evaluation in terms of average of total  $H_2$  and CO yield during the period of: (a) reduction and (b) oxidation steps of 10 MPO–CDS, MPO–WS, MPO–WS–CDS and MPO–CDS–WS cycles on pure nano-ceria and CV25. Error bars represent the deviation of maximum and minimum yield from the average yield value.

The stability test for pure nano-structured ceria and CV25 was performed through 100 cycles of the MPO–CDS and MPO–WS–CDS reactions. The fuel production rate yields per cycle and

5 cycles post 100 cycles are presented in Fig. 8 and S5.† A typical decline in the production rates and yields is observed in both oxygen carriers indicating possible sintering and incomplete



Fig. 8 Performance evaluation of CV25 during MPO–CDS and MPO–WS–CDS cycles: (a) and (b)  $H_2$  and CO production rates during 100 cycles; (c) and (d) average yield calculated after each step of 5 cycles; (e) and (f) syngas production rates during 5 redox cycles performed after the "100 cycle stability test".

#### Paper

oxygen recovery (Fig. 8a, b, S5a and S5b†). The fuel yield is calculated by taking the average yield over 5 cycles during the run of 100 cycles. A 47% and 63% increase in the fuel yield is observed in CV25 over pure nano-structured ceria during MPO-CDS and MPO-WS-CDS redox cycles, respectively, as shown in Fig. 8c, d, S5c and S5d.† The long-term stability test of the pure nano-structured ceria and CV25 was further investigated by measuring the oxygen exchange capacity by performing 5 cycles of MPO-CDS and MPO-WS-CDS reactions after the 100 redox cycles. Notably, the H<sub>2</sub> and CO production rates of pure nanostructured ceria and CV25 were largely unchanged and maintained a high performance, similar to the as-prepared material, as shown in Fig. 8e, f, S5e and S5f.†

The structural reorganization of the materials under investigation was evaluated by the determination of specific surface area and pore volume *via* BET analysis, before and after 100 cycles. The as-prepared nano-structured ceria possessed a higher specific surface area of  $81.77 \text{ m}^2 \text{ g}^{-1}$  compared to that of CV25 with a surface area of  $65.25 \text{ m}^2 \text{ g}^{-1}$ . Despite a 79% decline in surface area, CV25 exhibited a high and consistent oxygen exchange capacity during and after the 100 cycles. On the other hand, a 92% decrease in the surface area in pure nanostructured ceria is observed after the 100-cycle test. This shows that vanadia–ceria multi-phase systems not only support the redox capability for fuel production, but also avoid drastic deterioration through structural re-organization.

Overall, the vanadia-ceria binary phase redox oxide performed better than pure nano-structured ceria by achieving 53% higher H<sub>2</sub> and 51% higher CO yields during the methane partial oxidation and a 47% higher CO yield in the CO<sub>2</sub> splitting step in MPO-CDS reactions over 100 cycles. High yields of H<sub>2</sub> and CO are achieved in CV25 during sequential WS and CDS reactions (MPO-WS-CDS), with a 48% and 45% increase respectively, when compared to pure nano-structured ceria. The H<sub>2</sub> and CO yields during the reduction and oxidation reactions of MPO-WS-CDS and IGS-WS-CDS cycles is tabulated in Table 2 and compared to the current benchmark material (ceria) and other redox oxides reported recently, where MPO-driven reduction of oxygen carriers results in higher reduction extents with efficient syngas yields, a controlled H<sub>2</sub>/CO ratio  $(\sim 2)$  is another important aspect of an effective syngas production process. Notably, a mass-specific CO yield of 91 mL  $g^{-1}$  is achieved with CV25 samples during CO<sub>2</sub> splitting (e.g. 70% higher than the recently reported CO yield on La<sub>0.6</sub>Ca<sub>0.4</sub>-MnO<sub>3</sub> during reverse water gas shift reactions<sup>62</sup>), which is attributed to the extraordinary oxygen exchange capacity of CV25. Gao *et al.* reported a high CO yield of 397 mL  $g^{-1}$  during the CO<sub>2</sub> splitting step carried out for over 70 min.<sup>1</sup>

However, the long reduction durations resulted in a high  $H_2/CO$  ratio of 4.47, which deviates significantly from the  $H_2/CO$  ratio (*i.e.* 2) required for an ideal methane partial oxidation reaction. Pure nano-structured ceria in this study depicted

Table 2Performance comparisons of solar fuel production by oxygen carriers evaluated in this study and other benchmark materials reportedrecently. $t_c$ : operating time;  $N_c$ : number of cycles;  $T_{red}$ : reduction temperature;  $T_{ox}$ : oxidation temperature;  $Y_{H_2}$ : hydrogen yield;  $Y_{CO}$ : CO yield;WS: water splitting; CDS : CO2 splitting; MPO: methane partial oxidation; IGS: inert gas sweeping; RWGS: reverse water gas shift; FBAR: fixed bedalumina reactor; PCTSR: porous ceria tube solar reactor; CRSR: cavity receiver solar reactor; FBQR: fixed bed quartz reactor; FBR: fixed bedreactor; SD-TGA: solar driven thermo-gravimetric analysis; MRS: micro-reactor system; FBR<sup>a</sup>: fluidized bed reactor; SFR: stagnation flow reactor;QUTR: quartz U-tube reactor

				Reduction Oxidation								
Material	Process	$t_{\rm c}$ (h)	N <sub>c</sub> (#)	T <sub>red</sub> (K)	$Y_{\mathrm{H}_2}$ mL g <sup>-1</sup>	$Y_{\rm CO}$ mL g <sup>-1</sup>	$T_{\mathrm{OX}}(\mathbf{K})$	$Y_{\mathrm{H}_2}$ mL g <sup>-1</sup>	$Y_{\rm CO}$ mL g <sup>-1</sup>	$H_2$ : CO	Reactor type	Ref.
CeO <sub>2</sub>	MPO-CDS	66.7	100	1173	122	58	1173	_	49	2.09	FBAR	This work
CeO <sub>2</sub>	MPO-WS-CDS	66.7	100	1173	168	79	1173	71	_	2.14	FBAR	This work
25% V·CeO <sub>2</sub>	MPO-CDS	66.7	100	1173	261	118	1173	_	91	2.18	FBAR	This work
$25\% V \cdot CeO_2$	MPO-WS	6.7	10	1173	665	230	1173	160	5	2.89	FBAR	This work
$25\% V \cdot CeO_2$	MPO-WS-CDS	66.7	100	1173	320	145	1173	220	2	2.21	FBAR	This work
CeO <sub>2</sub>	IGS-WS	167	500	1773			1073	14	_	_	PCTSR	3
CeO <sub>2</sub>	IGS-WS-CDS	>8	10	1700	_	_	1100	2	0.9	_	CRSR	56
CeO <sub>2</sub>	MPO-CDS	12	10	1173	81	39	1173	_	55	2.09	FBAR	25
CeO <sub>2</sub>	MPO-CDS	46.7	100	1173	44	16	1173		35	2.74	FBAR	1
$3\% \text{ Ce} \cdot \text{Mn}_3\text{O}_4$	MPO-CDS	46.7	100	1173	77	20	1173	_	29	3.47	FBAR	1
3% Ce·Mn <sub>3</sub> O <sub>4</sub>	MPO-CDS	11.7	4	1173	640	143	1173	_	397	4.47	FBAR	1
$3\% \text{ Ce} \cdot \text{Mn}_3\text{O}_4$	MPO-WS	2	2	1173	846	253	1173	254	81	3.34	FBAR	1
$Ce_{0.8}Zr_{0.2}O_2$	MPO-WS	>2.7	1	973	29	14	773	19	_	2.08	FBQR	57
$Ce_{0.7}Fe_{0.3}O_3$	MPO-WS	>6.3	10	1123	27	14	973	23	_	1.89	FBR	28
CeO <sub>2</sub> /SiC	MPO-WS	0.7	3	1273	17	10	1273	27	_	1.72	SD-TGA	58
Fe <sub>3</sub> O <sub>4</sub>	MPO-WS	15.5	6	1223	159	79	1123	117	_	2.00	FBR	35
LaFeO <sub>3</sub> /CeO <sub>2</sub>	MPO-WS	> 27	30	1073	45	6	1073	5	_	7.40	MRS	16
LaFe <sub>0.9</sub> Ni <sub>0.1</sub> O <sub>3</sub>	MPO-WS		10	1123	_	_	1123	150	_	_	<b>FBR</b> <sup>a</sup>	59
CoFe <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	IGS-WS	4.6	3	1623	_	_	1623	2	_	_	SFR	60
Sr <sub>0.6</sub> La <sub>0.4</sub> Mn <sub>0.6</sub> Al <sub>0.4</sub> O <sub>3</sub>	IGS-CDS	40	80	1623	_	_	1273	_	3	_	SFR	61
La <sub>0.6</sub> Ca <sub>0.4</sub> MnO <sub>3</sub>	RWGS	3.3	5	823	—	—	823	—	28	—	QUTR	62



Fig. 9 Proposed mechanism for the contribution of CeO<sub>2</sub> and CeVO<sub>4</sub> during reduction and oxidation reaction for high syngas production than pure ceria.

a higher  $H_2$  and CO yield of 122 mL g<sup>-1</sup> and 58 mL g<sup>-1</sup>, while retaining the  $H_2/CO$  ratio close to 2, as compared to other reported ceria structures.<sup>1,25</sup> However, the multi-phase vanadiaceria system outperformed the pure nano-structured ceria by producing  $H_2$  (261 mL g<sup>-1</sup>) and CO (118 mL g<sup>-1</sup>) with a  $H_2/CO$ ratio of 2.18 during the MPO reaction and 91 mL g<sup>-1</sup> of CO in the oxidation step of 100 cycles of MPO-CDS reactions. Improved water splitting yields are observed with the combination of CDS reaction on CV25 over the 100 cycles with a maximum  $H_2/CO$  ratio of 2.21 when compared to MPO-WS with a  $H_2/CO$  ratio of 2.89 in pure nano-structured ceria.

### 4. Discussion

Ceria possesses high bulk oxygen mobility in its nonstoichiometric cubic structure and is efficient in creating oxygen vacancies upon reduction. Matta et al.37 have reported poor ethane oxidation on ceria-supported vanadia at 550 °C. Addition of vanadia up to 5 wt% loading in ceria results in deterioration in the catalytic activity of ceria. The high density of surface vanadia readily reacts with ceria and forms CeVO<sub>4</sub>, which may not be a fully reversible reaction due to oxygen leaching. Ceria exists in both 3+ (CeVO<sub>4</sub>) and 4+ (CeO<sub>2</sub>) oxidation states in ceria-vanadia multi-phase systems due to segregated phases of  $CeVO_4$  and  $CeO_2$ . The formation reaction of CeVO<sub>4</sub> also gives a  $\frac{1}{2}$  oxygen molecule towards the methane oxidation and results in the CeVO<sub>3</sub> phase consisting of Ce<sup>4+</sup> and  $V^{3+}$ , where re-oxidation of CeVO<sub>3</sub> consumes oxygen from the oxidation medium and forms CeVO4 and re-oxidized ceria. Consequently, co-existence of CeO<sub>2</sub> and CeVO<sub>4</sub> results in more oxygen species for reduction and oxidation reactions compared to pure ceria. The high density of surface vanadia species contributes the most in the formation of CeVO<sub>4</sub> because of its high extent of reduction,<sup>40</sup> whilst the V<sup>5+</sup> species interact with the ceria and promote its reduction from Ce<sup>4+</sup> to Ce<sup>3+</sup>, depending upon the reducing power of hydrocarbon and  $V^{\text{5+}}$ loading. The re-oxidation of cerium vanadate occurs via oxygen buffering by cerium, where cerium assists the re-oxidation of the reduced metal oxide system.40,49-55,63-65 Moreover, the interaction of surface vanadia with ceria stabilizes the surface Ce<sup>3+</sup>

by modulating the valence change in  $C^{4+}/Ce^{3+}$  due to the cyclic formation of CeVO<sub>4</sub> to CeVO<sub>3</sub>, which potentially can suppress the combustion of hydrocarbons during the redox cycles.<sup>41</sup> Hence, the co-existence of CeO<sub>2</sub> and CeVO<sub>4</sub> phases demonstrates a synergic effect in the redox reactions resulting in better syngas yields as compared to pure ceria, as shown in Fig. 9.

### 5. Conclusions

Facile and low-cost synthesis of oxygen carriers, possessing extraordinary oxygen ion mobility coupled with superior catalytic properties may lead to broad acceptance for use in thermochemical fuel production with high redox rates. This study is the first demonstration of the vanadia-ceria two phase system for thermochemical fuel production via methane partial oxidation followed by CO2, H2O, CO2-H2O and H2O-CO2 splitting. Suitable amounts of vanadium in CeO<sub>2</sub> results in a multiphase system consisting of CeO<sub>2</sub> and CeVO<sub>4</sub>, which increases syngas production rates by 68% during H<sub>2</sub>O splitting and 47% CO<sub>2</sub> splitting reactions, when compared to pure nanostructured ceria. Efficient re-oxidation of CeVO3 to CeVO4 plays a critical role in order to obtain high syngas yields, which is achieved by coupling H<sub>2</sub>O and CO<sub>2</sub> splitting reactions. The long-term cycling performance of these redox oxide pairs demonstrates that the oxygen exchange in the vanadia-ceria system during the redox reactions is highly reversible and can be performed up to hundred cycles, while maintaining high redox rates. In conclusion, these findings provide evidence that these binary phase systems can be used for the large-scale fuel production via improved thermochemical redox cycles.

### Funding

This project was supported by the Australian Research Council (ARC Future Fellowship FT140101213 by W. Lipiński).

## Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This study used the facilities and the scientific and technical assistance at the Centre of Advanced Microscopy at the Australian National University. We are grateful to Dr Michael Gao, Colin Carvolth and Kevin Carvolth for their assistance with setting up the IR furnace experiments.

### References

- 1 X. Gao, G. Liu, Y. Zhu, P. Kreider, A. Bayon, T. Gengenbach, T. Lu, Y. Liu, J. Hinkley, W. Lipiński and A. Tricoli, *Nano Energy*, 2018, **50**, 347–358.
- 2 C. Agrafiotis, M. Roeb and C. Sattler, *Renewable Sustainable Energy Rev.*, 2015, **42**, 254–285.
- 3 W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile and A. Steinfeld, *Science*, 2010, **330**, 1797–1801.
- 4 A. Steinfeld, Sol. Energy, 2005, 78, 603-615.
- 5 C. L. Muhich, B. D. Ehrhart, I. Al-Shankiti, B. J. Ward, C. B. Musgrave and A. W. Weimer, *Wiley Interdiscip. Rev.: Energy Environ.*, 2016, 5, 261–287.
- 6 J. R. Scheffe and A. Steinfeld, *Mater. Today*, 2014, **17**, 341–348.
- 7 R. J. Carrillo and J. R. Scheffe, Sol. Energy, 2017, 156, 3-20.
- 8 F. Call, M. Roeb, M. Schmücker, C. Sattler and R. Pitz-Paal, *J. Phys. Chem. C*, 2015, **119**, 6929–6938.
- 9 R. Bader and W. Lipiński, in Advances in Concentrating Solar Thermal Research and Technology, ed. M. J. Blanco and L. R. Santigosa, Woodhead Publishing, Amsterdam, 1st edn, 2017, pp. 403–459.
- 10 A. Riaz, P. Kreider, F. Kremer, H. Tabassum, J. S. Yeoh, W. Lipiński and A. Lowe, ACS Appl. Energy Mater., 2019, 2, 2494–2505.
- 11 P. T. Krenzke, J. R. Fosheim and J. H. Davidson, *Sol. Energy*, 2017, **156**, 48–72.
- 12 C. Agrafiotis, H. Von Storch, M. Roeb and C. Sattler, *Renewable Sustainable Energy Rev.*, 2014, **29**, 656–682.
- 13 M. Luo, Y. Yi, S. Wang, Z. Wang, M. Du, J. Pan and Q. Wang, Renewable Sustainable Energy Rev., 2018, 81, 3186–3214.
- 14 L. Protasova and F. Snijkers, Fuel, 2016, 181, 75-93.
- 15 Y. Zheng, K. Li, H. Wang, X. Zhu, Y. Wei, M. Zheng and Y. Wang, *Energy Fuels*, 2016, **30**, 638–647.
- 16 Y. Zheng, K. Li, H. Wang, D. Tian, Y. Wang, X. Zhu, Y. Wei, M. Zheng and Y. Luo, *Appl. Catal.*, *B*, 2017, **202**, 51–63.
- 17 D. Kang, M. Lee, H. S. Lim and J. W. Lee, *Fuel*, 2018, 215, 787–798.
- 18 K. Otsuka, Y. Wang, E. Sunada and I. Yamanaka, J. Catal., 1998, 175, 152–160.
- 19 P. T. Krenzke and J. H. Davidson, *Energy Fuels*, 2014, 28, 4088-4095.
- 20 R. Bader, L. J. Venstrom, J. H. Davidson and W. Lipiński, *Energy Fuels*, 2013, **27**, 5533–5544.
- 21 M. E. Dry, J. Chem. Technol. Biotechnol., 2002, 77, 43-50.
- 22 S. Abanades, A. Legal, A. Cordier, G. Peraudeau, G. Flamant and A. Julbe, *J. Mater. Sci.*, 2010, **45**, 4163–4173.
- 23 P. Singh and M. S. Hegde, Chem. Mater., 2010, 22, 762-768.

- 24 S. M. Haile and W. C. Chueh, *US Pat.* 8480923B2, 2009, vol. 1, pp. 1–17.
- 25 X. Gao, A. Vidal, A. Bayon, R. Bader, J. Hinkley, W. Lipiński and A. Tricoli, *J. Mater. Chem. A*, 2016, 4, 9614–9624.
- 26 L. J. Venstrom, N. Petkovich, S. Rudisill, A. Stein and J. H. Davidson, *J. Sol. Energy Eng.*, 2012, **134**, 011005–011012.
- 27 W. T. Gibbons, L. J. Venstrom, R. M. De Smith, J. H. Davidson and G. S. Jackson, *Phys. Chem. Chem. Phys.*, 2014, 16, 14271–14280.
- 28 X. Zhu, H. Wang, Y. Wei, K. Li and X. Cheng, *J. Rare Earths*, 2010, **28**, 907–913.
- 29 Y. Zheng, X. Zhu, H. Wang, K. Li, Y. Wang and Y. Wei, *J. Rare Earths*, 2014, **32**, 482–848.
- 30 D. J. Keene, W. Lipiński and J. H. Davidson, *Chem. Eng. Sci.*, 2014, **111**, 231-243.
- 31 Q. Jiang, J. Tong, G. Zhou, Z. Jiang, Z. Li and C. Li, *Sol. Energy*, 2014, **103**, 425–437.
- 32 W.-S. Dong, H.-S. Roh, K.-W. Jun, S.-E. Park and Y.-S. Oh, *Appl. Catal.*, *A*, 2002, **226**, 63–72.
- 33 F. He, Y. Wei, H. Li and H. Wang, *Energy Fuels*, 2009, 23, 2095–2102.
- 34 X. Zhu, Y. Wei, H. Wang and K. Li, *Int. J. Hydrogen Energy*, 2013, **38**, 4492-4501.
- 35 C. Lu, K. Li, H. Wang, X. Zhu, Y. Wei, M. Zheng and C. Zeng, *Appl. Energy*, 2018, **211**, 1–14.
- 36 D. Yamaguchi, L. Tang, L. Wong, N. Burke, D. Trimm, K. Nguyen and K. Chiang, *Int. J. Hydrogen Energy*, 2011, 36, 6646–6656.
- 37 J. Matta, D. Courcot, E. Abi-Aad and A. Aboukaïs, *Chem. Mater.*, 2002, 14, 4118–4125.
- 38 V. V. Guliants, Catal. Today, 1999, 51, 255-268.
- 39 T. Kodama, H. Ohtake, S. Matsumoto, A. Aoki, T. Shimizu and Y. Kitayama, *Energy*, 2000, 25, 411–425.
- 40 M. V. Martínez-Huerta, G. Deo, J. L. G. Fierro and M. A. Bañares, *J. Phys. Chem. C*, 2007, **111**, 18708–18714.
- 41 M. V. Martínez-Huerta, J. M. Coronado, M. Fernández-García, A. Iglesias-Juez, G. Deo, J. L. G. Fierro and M. A. Bañares, *J. Catal.*, 2004, 225, 240–248.
- 42 J. Hou, H. Huang, Z. Han and H. Pan, *RSC Adv.*, 2016, 6, 14552–14558.
- 43 X. Gao, I. Di Bernardo, P. B. Kreider, T. Tran-phu, X. Cai, N. Wang, J. Lipton-duffin, A. Bayon, W. Lipiński and A. Tricoli, ACS Catal., 2019, 9, 9880–9890.
- 44 Y. Y. Luo, D. S. Jo, K. Senthil, S. Tezuka, M. Kakihana, K. Toda, T. Masaki and D. H. Yoon, *J. Solid State Chem.*, 2012, 189, 68–74.
- 45 D. R. Mullins, S. H. Overbury and D. R. Huntley, *Surf. Sci.*, 1998, **409**, 307–319.
- 46 J. M. Vohs, T. Feng and G. S. Wong, *Catal. Today*, 2003, **85**, 303–309.
- 47 M. Lamers, S. Fiechter, D. Friedrich, F. F. Abdi and R. Van De Krol, *J. Mater. Chem. A*, 2018, **6**, 18694–18700.
- 48 C. A. Carrero, C. J. Keturakis, A. Orrego, R. Schomäcker and I. E. Wachs, *Dalton Trans.*, 2013, 42, 12644–12653.
- 49 N. Das, H. Eckert, H. Hu, I. E. Wachs, J. F. Walzer and F. J. Feher, *J. Phys. Chem.*, 1993, 97, 8240–8243.

- 50 Z. Wu, A. J. Rondinone, I. N. Ivanov and S. H. Overbury, *J. Phys. Chem. C*, 2011, **115**, 25368–25378.
- 51 A. Serrano-Lotina and L. Daza, *Int. J. Hydrogen Energy*, 2014, **39**, 4089–4094.
- 52 K. Zhao, F. He, Z. Huang, A. Zheng, H. Li and Z. Zhao, *Chin. J. Catal.*, 2014, **35**, 1196–1205.
- 53 A. Serrano-Lotina and L. Daza, *Appl. Catal.*, *A*, 2014, 474, 107–113.
- 54 M. Zhu, S. Chen, S. Ma and W. Xiang, *Chem. Eng. J.*, 2017, **325**, 322–331.
- 55 P. Cho, T. Mattisson and A. Lyngfelt, *Ind. Eng. Chem. Res.*, 2005, 44, 668–676.
- 56 P. Furler, J. R. Scheffe and A. Steinfeld, *Energy Environ. Sci.*, 2012, **5**, 6098–6103.
- 57 K. Otsuka, Y. Wang and M. Nakamura, *Appl. Catal., A*, 1999, 183, 317–324.
- 58 M. M. Nair and S. Abanades, *Energy Fuels*, 2016, **30**, 6050-6058.

- 59 Y. Shen, K. Zhao, F. He and H. Li, *J. Energy Inst.*, 2019, **92**, 239–246.
- 60 C. L. Muhich, B. W. Evanko, K. C. Weston, P. Lichty, X. Liang,
  J. Martinek, C. B. Musgrave and A. W. Weimer, *Science*, 2013,
  341, 540–542.
- 61 A. H. McDaniel, E. C. Miller, D. Arifin, A. Ambrosini, E. N. Coker, R. O'Hayre, W. C. Chueh and J. Tong, *Energy Environ. Sci.*, 2013, 6, 2424–2428.
- 62 D. Maiti, B. J. Hare, Y. A. Daza, A. E. Ramos, J. N. Kuhn and V. R. Bhethanabotla, *Energy Environ. Sci.*, 2018, **11**, 648–659.
- 63 E. Abi-aad, R. Bechara, J. Grimblot and A. Aboukaïs, *Chem. Mater.*, 1993, **5**, 793-797.
- 64 M. V. Martínez-Huerta, G. Deo, J. L. G. Fierro and M. A. Bañares, J. Phys. Chem. C, 2008, 112, 11441–11447.
- 65 C. Popa, M. V. Ganduglia-Pirovano and J. Sauer, J. Phys. Chem. C, 2011, 115, 7399-7410.