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Rh-doped ceria: solar organics from H₂O, CO₂ and sunlight?

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Abstract

The depleting supply of fossil fuels and rapidly increasing emissions of anthropogenic greenhouse gases demand sustainable solutions to the unfolding energy and environmental crises. One solution is to store concentrated solar energy in the form of chemical fuels via thermochemical cycles, which produce synthesis gas, a gas mixture of H₂ and CO that is the precursor of liquid fuels in the Fischer-Tropsch (FT) processes. To date, research efforts in this field have been devoted exclusively to the improvement of synthesis gas production, and no reports are available in direct generation of organic fuels such as methane and ethanol from H₂O and CO₂ by solar thermochemical cycles. With the aim to generate higher grade fuels directly from H₂O and CO₂ via thermochemical processes, we incorporate FT catalysts into the ceria lattice. In this study, we have synthesized rhodium doped ceria by coprecipitation. X-ray powder diffraction (XRD) indicates that the as-synthesized Rh-doped ceria is single-phased. High temperature XRD reveals that the Rh-doped ceria sustains its fluorite structure even at elevated temperatures up to 1400°C, indicating excellent structural stability highly desired for thermochemical cycles. The formation of oxygen vacancies in ceria due to the substitution of cerium by the lower valent rhodium cations is evidenced by Raman spectra. Rh-doped ceria exhibits an enhanced oxygen storage capacity (OSC) and superior activities in the conversion of H₂ and CO₂ into methane. These demonstrate great potential of Rh-doped ceria for the production of methane and other chemicals during the reoxidation in a thermochemical cycle, when H₂O, instead of H₂, is co-fed with CO₂. In fact, evidence strongly indicates that the H₂ produced from the splitting of H₂O is partly consumed when both H₂O and CO₂ are used for the reoxidation of thermally reduced Rh-doped ceria. Therefore the formation of higher grade fuels seems highly likely.

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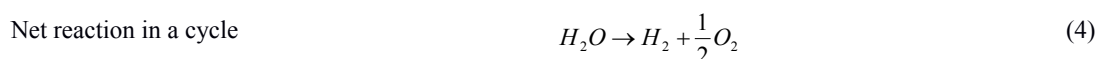
Keywords: thermochemical cycles; ceria; water splitting; solar fuels; organics; rhodium

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1. Introduction

Ceria (CeO_2) and related oxides (i.e. doped ceria) are among the most important non-stoichiometric functional oxides with widespread applications in environment-related and energy-related fields. This is mainly due to its inherent oxygen storage capacity (OSC) [1,2], i.e. the ability to store oxygen under oxidizing conditions and release oxygen under reducing conditions. Owing to this property, they are notably used as catalysts themselves or as support oxides in three-way catalytic converters in automobiles to combat harmful pollutants including CO and NO_x [3-7]. To our interest, recently ceria has also been studied as an active redox material for solar-driven two-step thermochemical cycles for the production of synthesis gas, namely solar fuels, from H_2O and CO_2 [8-10]. Thermochemical cycles for hydrogen production based on ceria were firstly demonstrated at a lab-scale by Abanades and Flamant [8]. Using a solar cavity reactor, Chueh and Steinfeld et al. demonstrated impressive rates of H_2 and CO production from the dissociation of H_2O and CO_2 respectively under realistic concentrated radiation and operating conditions relevant to industrial implementations [9]. These works are based on a concept of two-step cycles with ceria. In the first step, ceria is exposed to very high temperatures (i.e. generated from concentrated solar radiation) in an inert atmosphere and thus is thermally reduced. The temperature is usually 1500°C and higher in order to obtain decent degree of reduction. In the second step, the temperature is lowered (typically $<1100^\circ\text{C}$), and a flow containing gaseous H_2O and/or CO_2 is introduced to react with thermally reduced ceria, forming H_2 and/or CO. Ceria is oxidized to its original state and the cycle is completed. The net reaction in a cycle is therefore $\text{H}_2\text{O}/\text{CO}_2$ splitting. The following equations summarize the whole process.



The synthesis gas produced can be further converted to higher grade fuels such as methane and liquid hydrocarbons via Fischer-Tropsch (FT) processes. Due to the two-step nature, ceria-based thermochemical cycles bypass the CO/O_2 or H_2/O_2 separation as required in the case of direct thermal dissociation of CO_2 or H_2O . Since ceria stays solid-state during the cycle, no quenching step is required in comparison to ZnO-based cycles [11], thus allowing higher conversion efficiencies. From the equations, it is easy to see that the amount of synthesis gas produced in a cycle is directly determined by the extent of reduction (δ).

Very high temperature ($>1500^\circ\text{C}$) is required for thermal reduction of pure ceria, which is impractical and very disadvantageous from engineering perspectives. In order to achieve reduction of ceria at lower temperatures and thus increase solar fuel production after thermal reduction at a given temperature, doping ceria with heterocations has been investigated. Computational studies have shown that transition metal and noble metal ion substitution in ceria significantly enhances its reducibility and OSC [12,13], which could result in improved performances in solar H_2/CO production of doped ceria as reported in many previous studies [14-20].

Research efforts so far have been devoted exclusively to the improvement of synthesis gas production. To date, to the best of our knowledge there are no reports in direct generation of organic fuels such as methane and ethanol from H_2O and CO_2 by thermochemical cycles with thermal reduction. Such concept inherently bypasses the subsequent FT process, which could be more economically feasible as it does not require additional storage or transportation of syngas, or FT plants. Only very recently, Cheuh and Haile et al. demonstrated the direct formation of methane from H_2O and CO_2 , using 10 wt% metallic nickel on samarium-doped ceria [21]. However, H_2 was used to assist the reduction of ceria at much lower temperatures compared to the case of thermal reduction, which would quickly degrade the materials due to severe sintering of nickel metals at high reduction temperatures.

With the aim to generate methane and liquid fuels directly from H₂O and CO₂ via thermochemical processes, we here propose a strategy of incorporating the FT processes into a thermochemical cycle by doping ceria with a FT catalyst. Taking rhodium as an example, many studies have been carried out on the conversion of synthesis gas to methane, methanol, ethanol and other higher oxygenates using metallic rhodium dispersed on oxide supports. There are only few reports on the incorporation of rhodium cations into the support lattice structure [22-24], despite the potential advantages such as very high dispersion, and thus high number of active reaction sites [22,23]. Conceptually, cationic rhodium will play two roles in this system. One is to improve the oxygen storage capacity of ceria, and thus increase fuel production. The other role is to serve as catalytic sites during the reoxidation to produce organic molecules. The formation of these organic fuels can be either from the conversion of the synthesis gas generated by H₂O/CO₂ splitting, or directly from H₂O/CO₂ without the intermediate formation of synthesis gas, or a combination of both. In this study, we have incorporated cationic rhodium into the ceria lattice using a simple coprecipitation method. We will reveal by high temperature X-ray diffraction (XRD) that such single-phased Rh-doped ceria sustains its fluorite structure even at elevated temperatures up to 1400°C, indicating excellent structural stability highly desired for thermochemical cycles. We will also show that the incorporation of rhodium into the ceria lattice, evidenced by Raman spectroscopy, enhances the reducibility of ceria. We will then demonstrate the potential of Rh-doped ceria for the production of methane and other chemicals during the reoxidation step of a thermochemical cycle, when H₂O and CO₂ are used as oxidizing agents.

2. Methods

2.1. Materials Synthesis

Pure ceria (CeO₂) and Rh-doped ceria (Ce_{0.99}Rh_{0.01}O_{2-δ}) were synthesized by coprecipitation using ammonia as a precipitating agent. Ce(NO₃)₃·6H₂O (99.99%) and Rh(NO₃)₃·xH₂O (99.99%) from Sigma Aldrich were used as precursors without further purification. Stoichiometric quantities of the precursors were dissolved in excess amount of de-ionized water and stirred continuously. After complete dissolution, diluted aqueous ammonia solution (28 vol%) was added drop-wise into the golden precursor mixture, forming grey precipitates. The pH was monitored with a pH meter and the addition of ammonia solution was stopped when the pH of the mixture was stabilized at 9. Then the solution containing precipitates was aged for 24 h under constant stirring and allowed to settle for another 24 h. The precipitated solids were filtered and rinsed a few times until the pH of the effluent fell below 7. To prepare for calcination, the filter cake was dried at 80°C in static air for ~12 hours and then crushed in an agate mortar. The well-grinded fine powder was finally calcined at 500°C for 5 hours (heating rate 5°C/min). Pure ceria was synthesized according to the same procedure.

2.2. X-ray powder diffraction (XRD) and high temperature XRD

To identify the crystalline phases of all materials, room temperature XRD was carried out using an X'Pert diffractometer from PANalytical. In a typical measurement the sample was grinded with ethanol in an agate mortar and a few drops of the dispersion were deposited on a glass slide. The 2θ range was usually set as 20-80° with a step size of 0.05° and an integration time of 5 s. Cu K_α radiation with λ=1.5405 Å was used as X-ray source. For data analysis (i.e. identification of peak positions and peak widths), the diffraction patterns were processed with the PANalytical X'Pert HighScore software.

To study the structural stability of Rh-doped ceria *in-situ*, high temperature XRD studies were carried out using the same diffractometer equipped with an HDK2.4 chamber. The sample was prepared the same way but deposited on resistively heated platinum strips. Constant mechanical tension was applied on the platinum substrate in order to avoid buckling caused by thermal expansion when heated. A step size of 0.04° and an integration time of 7 s were set for all the patterns collected. The heating was set as 60°C min⁻¹ in ambient air.

2.3. Raman spectroscopy and thermogravimetry

In order to verify the incorporation of rhodium in the host lattice of ceria, Raman spectra of pure ceria and Rh-doped ceria were recorded with a Horiba Jobin Yvon HR 800 Raman spectrometer at room temperature and ambient pressure. The light source was generated by an Ar⁺ laser (633 nm). To focus the laser on the samples, an optical microscope was used.

Oxygen storage capacity (OSC) is a key feature of ceria and usually directly related to its catalytic properties. In order to study the effect of rhodium incorporation on the OSC of ceria, we carried out thermogravimetric (TG) studies with pure ceria and Rh-doped ceria using a Netzsch TA409 TG analyzer. The sample was dried under a vacuum of approximately 50 mbar at 200°C for an hour before being loaded to the analyzer. The temperature of the TG furnace was increased to 500°C at a rate of 20°C min⁻¹ under 10% O₂ in Ar and then maintained at this temperature. At 500°C the sample was subjected to alternating reducing (10% H₂ in Ar) and oxidizing (10% O₂ in Ar) conditions while the mass change was recorded. The total flow rate was kept at 100 ml min⁻¹ throughout the experiment.

2.4. CO₂ methanation and thermochemical H₂O-splitting

CO₂ methanation was studied at various temperatures in the TG reactor. The total gas flow was 25 ml min⁻¹, which was comprised of 5 ml min⁻¹ Ar, 5 ml min⁻¹ CO₂ and 15 ml min⁻¹ H₂. The temperature was increased stepwise from 350°C to 700°C. The effluent gases were analyzed and quantified by gas chromatography (GC), which recorded the concentrations of H₂, CO, CO₂, CH₄, O₂ and N₂ at a time interval of about 2 min every measurement. For comparison, pure ceria was also studied for its CO₂ methanation activity at temperatures between 350°C to 500°C.

To evaluate the potential of Rh-doped ceria as a redox material to directly convert H₂O and CO₂ into organic fuels via thermochemical cycles, we conducted thermochemical H₂O-splitting experiments in presence of CO₂. The experimental setup included three major parts: gas supply for reducing conditions (Ar) and oxidizing conditions (Ar/H₂O/CO₂), an alumina tube reactor housed in a programmable tube furnace, and a mass spectrometer for gas analysis. The thermal reduction was carried out at 1300°C under a flow rate of 80 ml min⁻¹ Ar, reoxidation at 500°C under a flow rate of 80 ml min⁻¹ Ar, 1 g h⁻¹ gaseous H₂O (equivalent to ~20.7 ml min⁻¹) and 10 ml min⁻¹ CO₂. About 200 mg of Rh-doped ceria was used. The H₂ concentration was continuously monitored and recorded using the mass spectrometer.

3. Results and discussion

3.1. Structural stability of Rh-doped ceria at high temperatures

In Figure 1a room temperature XRD patterns of pure ceria and Rh-doped ceria after synthesis are presented. It is obvious that Rh-doped ceria only shows reflections characteristic of cubic fluorite-type ceria. The absence of reflections from Rh-related phases (i.e. RhO_x) suggests that rhodium is completely incorporated into the host lattice of ceria. In addition, Rh-doped ceria also exhibits lower reflection intensities relative to pure ceria, indicating reduced crystallinity. Estimation based on Scherrer's equation shows a slight decrease of crystallite sizes to 11.8±1.4 nm for Rh-doped ceria (14.1±3.1 nm for pure ceria). For Rh-doped ceria to fulfill its intended high temperature application as an active redox material for solar-driven thermochemical cycles, structural stability is a key factor and the material must sustain its single-phased structure after repeated exposure to high temperatures. To evaluate the structural stability of Rh-doped ceria, it was subjected to high temperature heat treatment at 1300°C for 24 h in air. The XRD patterns of pure ceria and Rh-doped ceria after this treatment are presented in Figure 1b. Evident from the reduced peak widths the samples exhibit increased crystallinity due to sintering at high temperature for prolonged period of time. Both of the samples exhibit crystallite sizes of 49.6±2.2 nm. No Rh-related phases are detected by XRD, indicating that Rh-doped ceria is structurally stable at temperatures as high as 1300°C in air.

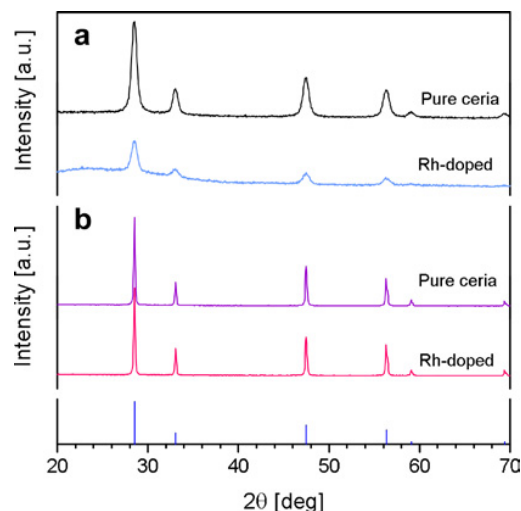


Fig. 1. Room XRD patterns of pure ceria and Rh-doped ceria as-calcined (a), and after additional heat treatment at 1300°C for 24 h. Stick pattern of ceria is included as well as a reference.

In order to further verify the structural stability of Rh-doped ceria, an *in-situ* high temperature XRD experiment was performed in air. Before heating was started, an XRD pattern was recorded at 30°C. Then XRD patterns were collected at every 200°C from 200°C to 1400°C, each measurement lasting approximately 3 h. All patterns exhibit reflections of cubic ceria and the Pt substrate. Features marked with empty circles observed at temperatures from 400°C to 1400°C must be artifacts considering that their intensities and positions show almost no change. Again, with increasing temperatures the peaks become narrower, indicating increasing crystallinity. Meanwhile all reflections shift to lower angles due to thermal expansion of the lattice. Rh-related phases are not observed. Thus it is suggested that we have successfully synthesized single-phased Rh-doped ceria with structural stability at high temperatures.

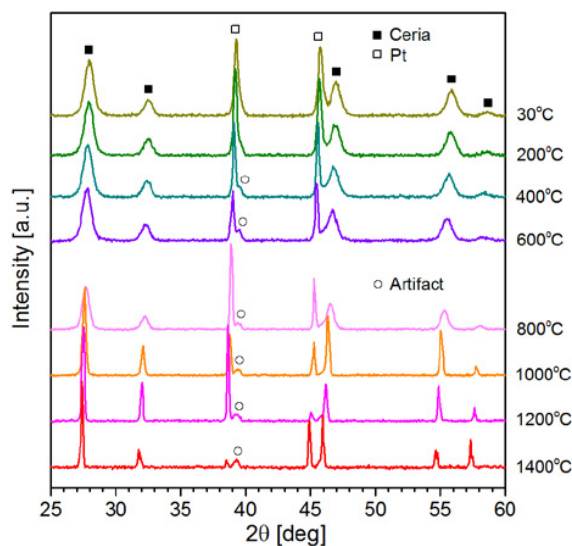


Fig. 2. *In-situ* high temperature XRD patterns of Rh-doped ceria in air. Filled square represents ceria phase and open square the substrate Pt. Features marked with open circles are artifacts.

3.2. Incorporation of rhodium and its effect on the OSC of ceria

Raman spectroscopy is widely used to characterize ceria-related materials in catalysis due to its sensitivity to lattice defects and perturbations caused by the dopants incorporated [25,26]. XRD suggests full incorporation of Rh into the host lattice of ceria. However due to the low doping level of only 1 mol%, peak shift caused by lattice contraction or expansion is not discernible from the XRD patterns. To verify the incorporation of rhodium, we carried out Raman spectroscopic studies with the pure ceria and Rh-doped ceria. The results are presented in Figure 3.

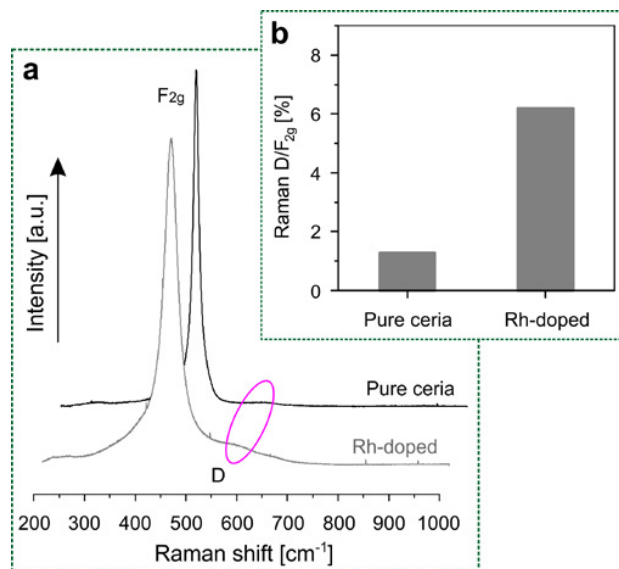


Fig. 3. Raman spectra of pure ceria and Rh-doped ceria as-calcined (a), and the corresponding Raman D/F_{2g} ratio (b) that is indicative of oxygen vacancy concentration within the material.

At first glance as seen in Figure 3a, both samples exhibit a prominent peak at about 450-460 cm⁻¹, which is the F_{2g} vibrational mode characteristic of cubic ceria. It is easy to observe that this peak is broadened for Rh-doped ceria in comparison to pure ceria. This proves that that rhodium is indeed incorporated into the ceria lattice, thus causing lattice perturbations and leading to the observed F_{2g} peak broadening [26]. Peaks associated with rhodium oxide, i.e. Rh₂O₃ [24] are not observed. The incorporation of rhodium (i.e. substitution of Ce⁴⁺ by the divalent Rh²⁺ or trivalent Rh³⁺) will lead to the formation of extrinsic oxygen vacancies within the ceria lattice to maintain charge balance. These charge compensating oxygen vacancies are evidenced by increased Raman intensity at around 600 cm⁻¹. The D band at this frequency is usually associated with oxygen vacancy defects within the ceria lattice [25]. In order to compare the oxygen vacancy concentrations between pure ceria and Rh-doped ceria, the D band intensity is normalized by the F_{2g} intensity and the results are presented in Figure 3b. Clearly the D/F_{2g} for Rh-doped ceria is more than 5 times the value of pure ceria, indicating a higher oxygen vacancy concentration.

To study the effect of rhodium incorporation on the OSC of ceria, we carried out thermogravimetric studies with pure ceria and Rh-doped ceria under alternating reducing (10% H₂/Ar) and oxidizing conditions (10% O₂/Ar) at 500°C. The relative weight losses (oxygen release) and mass gains (oxygen uptake) over three cycles are reported in Figure 4. For both of the two samples, oxidation of ceria occurs more rapidly than its reduction. Spikes in the recorded mass signals when the atmosphere is changed from oxidizing to reducing conditions (and *vice versa*) are due to incomplete compensation of buoyancy effects: ceria reacts with hydrogen and oxygen, and thus influences the gas composition. This effect can not be compensated in the buoyancy curve as ceria is not present. If we compare the TG curves between pure ceria and Rh-doped ceria, two clear differences emerge. The rate of reduction

for Rh-doped ceria is considerably higher than the rate for pure ceria. Considering that pure ceria and Rh-doped ceria exhibit very close crystallite sizes (see discussion of Figure 1), the faster reduction of Rh-doped ceria strongly indicates its enhanced reducibility due to the incorporation of rhodium in the host lattice. The other difference is that the mass losses and gains for Rh-doped ceria are higher than pure ceria. We do not observe the formation of metallic rhodium by *in-situ* high temperature XRD under identical conditions. Thus the mass losses and gains are attributed to the redox pair of $\text{Ce}^{4+}/\text{Ce}^{3+}$. Based on the relative weight gains over the three cycles, we calculated that Rh-doped ceria has an OSC of $206.1 \pm 3.7 \mu\text{mol-O g}^{-1}$, an increase of approximately 40% from the OSC of pure ceria ($146.6 \pm 6.4 \mu\text{mol-O g}^{-1}$). The increased OSC of Rh-doped ceria and its enhanced reducibility evident from more rapid reduction show the potential of Rh-doped ceria for improved solar fuel production.

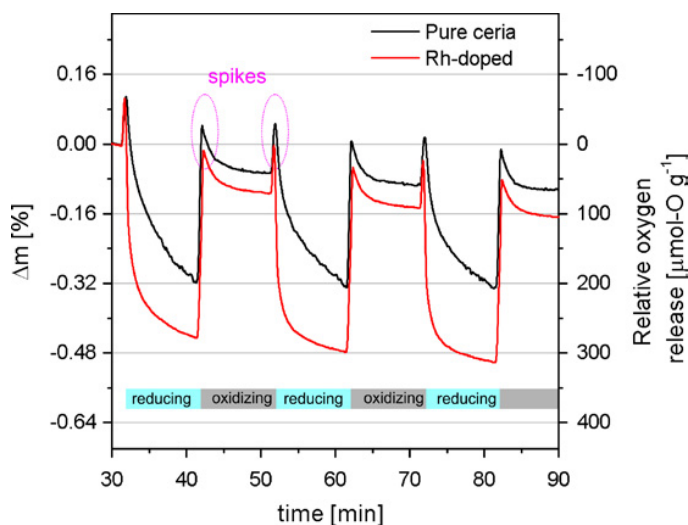


Fig. 4. Weight losses and gains in response to alternating reducing (10% H_2/Ar) and oxidizing conditions (10% O_2/Ar) at 500°C of pure ceria and Rh-doped ceria. Right vertical axis represents the amount oxygen release per g of materials relative to the starting point (at 30 min).

3.3. CO_2 methanation and thermochemical H_2O splitting

To evaluate the catalytic activity of Rh-doped ceria, we carried out CO_2 methanation experiments in the TG reactor. Pure ceria was also studied for comparison. Figure 5 shows the results of CO_2 hydrogenation at various temperatures for pure ceria (a) and Rh-doped ceria (b). Some activity for the reverse water-gas shift reaction is observed with pure ceria in the temperature range studied (350°C to 500°C). However, essentially no methane is formed. Although the conversion of CO_2 to CO via reverse water-gas shift reaction is limited with pure ceria, the extent is significantly enhanced with increasing temperatures. The conversion at 500°C is more than an order of magnitude higher than the conversion at 400°C . In contrast, Rh-doped ceria strongly promotes the formation of methane by CO_2 hydrogenation at temperatures between 350 - 500°C . As the temperature is further increased, methane formation is less favored and CO is preferred due to thermodynamics. Regarding the CO_2 to CO conversion via reverse water-gas shift reaction, Rh-doped ceria compared to pure ceria, is over 20 times more active at 400°C , and twice as active at 500°C . The results shown in Figure 5 indicate great potential of Rh-doped ceria in converting H_2O and CO_2 directly into methane via thermochemical cycles when the reoxidation is performed between 400 - 500°C .

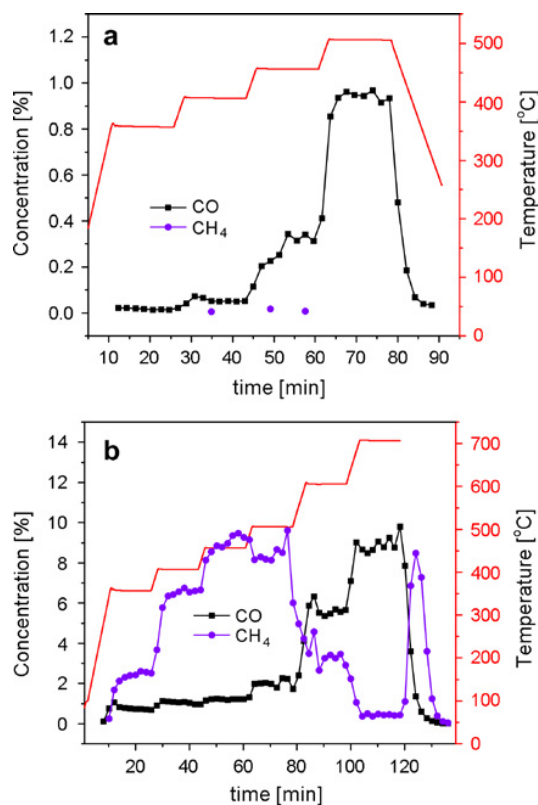


Fig. 5. Catalytic activities of pure ceria (a) and Rh-doped ceria (b) in converting CO₂ and H₂ into CH₄ at various temperatures.

With the aim to generate organic molecules such as methane directly from H₂O and CO₂ via thermochemical cycles, we thermally reduced Rh-doped ceria at 1300°C in Ar, and used a mixture of Ar/H₂O/CO₂ for reoxidation at 500°C. Zn-doped ceria, which is not active for CO₂ methanation (results not shown), was also studied under similar conditions for comparison. The difference between these two experiments is that the reoxidation was carried out at 1000°C with a mixture of Ar and H₂O (no CO₂ was used) for Zn-doped ceria. The results for Zn-doped ceria and Rh-doped ceria are presented in Figure 6a and 6b respectively. Both samples shows activities of H₂O-splitting after thermal reduction at 1300°C, 200-300°C lower than typical reduction temperatures of pure ceria [9,10]. The peak H₂ concentrations are ~0.3% and ~0.65% respectively for the two cycles with pure ceria, ~0.1% and ~0.25% respectively with Rh-doped ceria. The lower peak H₂ concentrations observed with Rh-doped ceria are due to smaller amount of materials used (200 mg). It seems that the H₂O-splitting activity increases within the first few cycles in both cases. However, more studies are needed to confirm this and its causes need to be investigated.

Furthermore, the H₂ signals recorded during the reoxidation of Zn-doped ceria by only H₂O exhibit a relatively slow decay in both cycles (see Figure 6a). It takes about 10-15 min for the H₂ signal to return to the background level. This is consistent with a previous study by Furler and Steinfeld et al. [10]. In contrast, the reoxidation of thermally reduced Rh-doped ceria by a mixture of gaseous H₂O and CO₂ shows a very rapid decay of the H₂ signal, as seen in Figure 6b. The H₂ signal quickly falls back to the background level within half a minute in both cycles despite that the reoxidation temperature is 500°C, much lower than the temperature for Zn-doped ceria (1000°C). The decaying rate of the H₂ signals for the Rh-doped ceria (despite a much lower reoxidation temperature) is 20-30 times that for the Zn-doped ceria. This strongly suggests that, in the case of Rh-doped ceria, part of the H₂ produced from the splitting of H₂O is not the final product and is consumed as intermediates. Recalling the results of CO₂ methanation shown in Figure 5, we believe that this consumption is likely due to CO₂ hydrogenation, and thus the formation of organic molecules seems highly likely.

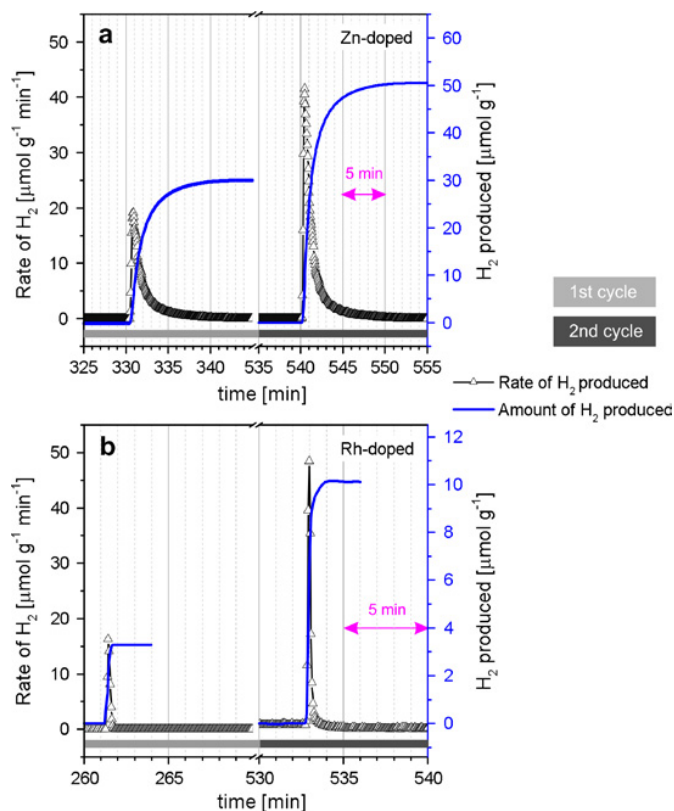


Fig. 6. H₂ evolution rates (black curves with open triangles) and cumulative H₂ production (blue curves) for two thermochemical cycles with Zn-doped ceria (a) and Rh-doped ceria (b).

Although beyond the scope of the present study, it is important to stress that for thermal reduction at temperatures higher than 1300°C, sublimation of rhodium over long-term thermochemical cycling shall be assessed. This could be of significant importance, considering the possibility of rhodium (oxide) separation from the ceria lattice. However, we found that thermochemical CO₂ splitting (1400°C/1000°C) with Rh-doped ceria shows enhanced and sustained activities in comparison to pure ceria over at least four cycles. This seems to suggest that the material is stable at even 1400°C, although testing over longer term is required. Thermal reduction beyond 1400°C can bring problems such as severe sintering, ceria sublimation and practical engineering issues, which are likely to outweigh the benefit of increased reduction extent. In fact, additional data from us shows that Rh-doped ceria already exhibits decent CO productivity of >140 μmol g⁻¹ per cycle, in comparison to the value for pure ceria after reduction at around 1600°C: ~180 μmol g⁻¹, calculated from a previous study by Chueh et al. [9].

4. Conclusions

In summary, our work shows great potential of Rh-doped ceria as a redox active material to convert H₂O and CO₂ directly into organic fuels, i.e. methane, via solar-driven thermochemical cycles. Nanocrystalline Rh-doped ceria synthesized by coprecipitation shows great structural stability at high temperatures up to 1400°C, a property highly desired for thermochemical cycles based on doped ceria. Raman spectroscopy evidences the incorporation of rhodium into the ceria lattice and the formation of charge compensating oxygen vacancies in the oxygen sub-lattice. Such incorporation of rhodium cations enhances the oxygen storage capacity of ceria, as revealed by thermogravimetric studies. Rh-doped ceria also shows superior activities for CO₂ methanation between 350°C and 500°C while pure ceria shows none. This finding indicates that if H₂ is replaced by H₂O and a thermal reduction step at high temperatures for ceria activation is introduced, it is feasible to produce methane directly from H₂O and CO₂

thermochemically. The reoxidation of thermally reduced Rh-doped ceria by a mixture of gaseous H₂O and CO₂ shows a decay of the H₂ signal at a rate 20-30 times as fast as the case of Zn-doped ceria, in which only H₂O (no CO₂) was used for reoxidation. This strongly indicates that, in the case of Rh-doped ceria, the H₂ produced is partly consumed, likely due to CO₂ hydrogenation. Thus the formation of organics such as methane seems highly likely.

Acknowledgements

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