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Solid-State Redox Kinetics of CeO_2 in Two-Step Solar CH_4 Partial Oxidation and Thermochemical CO_2 Conversion

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Abstract: The $\text{CeO}_2/\text{CeO}_{2-\delta}$ redox system occupies a unique position as an oxygen carrier in chemical looping processes for producing solar fuels, using concentrated solar energy. The two-step thermochemical ceria-based cycle for the production of synthesis gas from methane and solar energy, followed by CO_2 splitting, was considered in this work. This topic concerns one of the emerging and most promising processes for the recycling and valorization of anthropogenic greenhouse gas emissions. The development of redox-active catalysts with enhanced efficiency for solar thermochemical fuel production and CO_2 conversion is a highly demanding and challenging topic. The determination of redox reaction kinetics is crucial for process design and optimization. In this study, the solid-state redox kinetics of CeO_2 in the two-step process with CH_4 as the reducing agent and CO_2 as the oxidizing agent was investigated in an original prototype solar thermogravimetric reactor equipped with a parabolic dish solar concentrator. In particular, the ceria reduction and re-oxidation reactions were carried out under isothermal conditions. Several solid-state kinetic models based on reaction order, nucleation, shrinking core, and diffusion were utilized for deducing the reaction mechanisms. It was observed that both ceria reduction with CH_4 and re-oxidation with CO_2 were best represented by a 2D nucleation and nuclei growth model under the applied conditions. The kinetic models exhibiting the best agreement with the experimental reaction data were used to estimate the kinetic parameters. The values of apparent activation energies ($\sim 80 \text{ kJ}\cdot\text{mol}^{-1}$ for reduction and $\sim 10 \text{ kJ}\cdot\text{mol}^{-1}$ for re-oxidation) and pre-exponential factors ($\sim 2\text{--}9 \text{ s}^{-1}$ for reduction and $\sim 123\text{--}253 \text{ s}^{-1}$ for re-oxidation) were obtained from the Arrhenius plots.

Keywords: concentrated solar energy; ceria; oxygen carriers; thermochemical redox cycle; chemical-looping; methane reforming; syngas; solid-state kinetics; CO_2 utilization

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1. Introduction

Oxygen carriers based on nonstoichiometric metal oxides play prominent roles in the development of chemical looping processes, the two-step thermochemical splitting of $\text{H}_2\text{O}/\text{CO}_2$, air separation, thermochemical energy storage, and the chemical looping combustion (CLC) of hydrocarbon fuels [1–16]. Carrying out these reactions using concentrated solar energy (CSE) can be considered an effective strategy to utilize the entire solar energy spectrum, while avoiding the use of expensive precious metal catalysts. In general, thermochemical redox cycles involve a reduction of the oxygen carrier at high temperature in the first step. Here, the evolution of lattice oxygen takes place, resulting in the formation of a partially reduced phase of the oxygen carrier. Re-oxidation of the partially reduced metal oxide is then achieved using an oxidant (e.g., air, CO_2 , and H_2O) at comparatively lower temperatures in the second step [17]. $\text{CeO}_2/\text{CeO}_{2-\delta}$ is the most widely investigated nonstoichiometric redox system and oxygen carrier used for solar-driven thermochemical fuel production so far. Enhanced oxygen release and storage capacities, crystallographic structure stability during the Ce^{4+} to Ce^{3+} reversible reduction, and rapid reaction kinetics during thermochemical redox cycles make it attractive from a

commercial perspective [1–3]. Muhich et al. recently reported that isothermal redox cycles are more efficient than temperature-swing cycles for carrying out this process [18]. Indeed, isothermal redox cycles can be more attractive in processing time and energy conversion efficiency aspects [17,18]. Such isothermal or near-isothermal reaction conditions can be achieved by incorporating a hydrocarbon-based reducing agent (such as methane) in the first step of the redox cycle to lower the reduction temperature [2,19–25]. The entire reaction sequence can thus be conducted at the same temperature by coupling the partial oxidation of CH₄ with the ceria redox cycle. Moreover, this leads to a decrease in the operating temperature of the whole cycle, as both CH₄-induced reduction of the oxygen carrier and subsequent re-oxidation with CO₂ can proceed at a similar temperature, while producing additional CO and H₂ (syngas) during the ceria reduction step with methane.

Most of the previous studies so far have focused on using either pure or doped ceria to study the performance of these materials, and these studies clearly indicated that the active material synthesis method, surface microstructure, morphology, porosity, and presence of inert promotional agents can crucially influence the redox chemistry (including reaction selectivity and thermochemical stability) of such materials [1–3,19–25].

In parallel, information regarding reaction kinetics has also been obtained [26–31]. An appropriate kinetic model for the redox reactions incorporating nonstoichiometric oxygen carriers is strongly desired for rational reactor design purposes. In contrast to the general complexity in gas–solid reactions, the redox kinetic description of CeO₂ is comparatively simpler. This is because during the first reduction step, apart from producing oxygen vacancies in the solid oxygen carrier, a phase change is generally not involved. Different models have been used to describe the conversion profiles of such noncatalytic gas–solid thermochemical reactions [32–37]. The mechanism of solid-state reduction kinetics of CeO₂-Fe₂O₃ systems was found to vary depending on the amount of Fe₂O₃ [28]. LaFeO₃ and NiO oxygen carriers were found to follow a 2D nucleation and nuclei growth model for solid-state reduction in the presence of CH₄ [33,37]. Similar studies incorporating perovskites indicated that the solid-state mechanism for reduction and re-oxidation relied on the composition, temperature, and extent of conversion [31,34]. It has to be noted that the material compositions and the experimental conditions used by various authors may vary significantly. In addition, many of these studies were carried out using conventional thermogravimetric analyzers. Therefore, it is relevant to compare the applicability of different models in thermochemical redox reactions separately for individual oxygen carriers, to correlate the representative reactivity information obtained using an original solar reactor.

In this study, the solid-state kinetics and reaction mechanism of thermochemical reduction and re-oxidation reactions taking place over CeO₂ oxygen carriers were carefully monitored. Classical kinetic models, including the power law model (PLM), the shrinking core model (SCM), and the nucleation and nuclei growth model (NGM), were compared on the basis of their ability to accurately describe the experimental data [32–37]. Thermochemical reduction and re-oxidation cycles were carried out in the presence of CH₄ and CO₂, respectively. The amounts of oxygen being released and absorbed by the material during redox reactions were measured continuously, over commercial CeO₂ powder. The reactions were performed and investigated using a customized solar thermogravimetric reactor developed previously at PROMES-CNRS. The solar thermal reactor was installed at the focus of a parabolic dish concentrator to investigate the kinetics of solid–gas reactions at high temperatures [29]. The solid-state reduction and re-oxidation kinetics of CeO₂ oxygen carriers with CH₄ and CO₂ followed a 2D nucleation and nuclei growth model (R2), based on the kinetic data obtained in the developed solar thermogravimetric reactor.

2. Results and Discussion

Structural and morphological materials characterizations were performed. Powder X-ray diffraction (XRD) patterns were obtained for the commercial CeO_2 oxygen carrier. The observed reflections in the wide-angle region were in good agreement with the well-crystallized and phase-pure cubic CeO_2 with a fluorite structure. The obtained diffraction patterns are shown in Figure 1a. In the case of the material recovered after the reduction step, reflections corresponding to Ce_2O_3 and CeO_2 phases were found to co-exist, indicating the partial reduction of CeO_2 to $\text{CeO}_{2-\delta}$. Furthermore, the peaks corresponding to Ce_2O_3 disappeared in the material recovered after the re-oxidation step (presence of CeO_2 phase only), indicating that complete re-oxidation was achieved for this material under the conditions investigated in the present study. Average crystallite sizes were determined for the materials before and after redox cycling experiments by applying the Scherrer equation over the most intense reflection (111) peak of the XRD patterns ($2\theta = 28.5^\circ$). A moderate variation in size was observed for CeO_2 after pre-treatment at 1000°C (54.55 nm) in comparison with the material powder as received (40.4 nm). However, a further enhancement of the crystallite size was not observed for the materials recovered after one complete redox cycle (50.38 nm), indicating that the effect of sintering was negligible and structure stabilization was reached after the thermal pre-treatment. In conjugation, the information regarding surface microstructure and morphology were obtained from the scanning electron microscopy (SEM) images. Nano-sized primary particles with irregular morphologies and a nearly homogeneous size distribution were observed. These particles were found to be randomly agglomerated to form a dense network structure with domain sizes in the micrometer range. Representative images are provided in Figure 1b,c.

Figure 1. Characterization of ceria materials used in this study: (a) Powder X-ray diffraction (XRD) patterns of as-received fresh CeO_2 oxygen carriers (C-F), ceria after pre-treatment (C-P), ceria after reduction (C-R), and ceria used after one complete cycle (C-U), (*) denotes Ce_2O_3 phase; (b,c) SEM images of fresh CeO_2 oxygen carriers.

Thermochemical redox cycles, using concentrated solar energy, were then carried over these oxygen carriers in a solar thermochemical reactor (see Section 3 for experimental details on materials cycling). A significant amount of oxygen release was observed above 800 °C. Isothermal redox experiments were performed at selected temperatures (900, 1000, and 1050/1070 °C) and the corresponding O and CO evolution profiles (representing δ in $\text{CeO}_{2-\delta}$, according to Equations (1) and (2), and determined from the sample mass variation) are shown in Figure 2. This temperature range was selected to obtain noteworthy redox activity without compromising the thermal stability [21–25]. Moreover, higher temperatures would favor the direct thermal methane decomposition to hydrogen and solid carbon [38–40]. The CeO_2 sample was placed in the reaction chamber of the solar reactor under a flow of inert Ar ($0.5 \text{ L} \cdot \text{min}^{-1}$) during the heating step, and concentrated solar energy was used to provide process heat and reach the necessary reaction temperature.

Figure 2. Experimental O (a) and CO (b) evolution profiles as a function of time at selected temperatures and reactant partial pressures over CeO_2 oxygen carriers performed in a solar reactor using concentrated solar energy.

A continuous flow of CH_4 ($0.2 \text{ L} \cdot \text{min}^{-1}$, with an Ar flow rate of $0.3 \text{ L} \cdot \text{min}^{-1}$ corresponding to 40% CH_4 in Ar) was injected at constant temperature and was maintained until the oxygen-releasing step from ceria was completed. Partial oxidation of CH_4 took place from the released oxygen in this first step, leading to the formation of reduced ceria ($\text{CeO}_{2-\delta}$), along with syngas ($\text{CO} + \text{H}_2$). Previous studies clearly demonstrated that CeO_2 is highly selective toward the partial oxidation of CH_4 , producing syngas [19–25]. In the second step, the entire amount of CH_4 remaining inside the reactor was first removed using a vacuum pump, and CO_2 was subsequently injected ($0.2 \text{ L} \cdot \text{min}^{-1}$, with an Ar flow rate of $0.3 \text{ L} \cdot \text{min}^{-1}$ corresponding to 40% CO_2 in Ar), while maintaining the same temperature in order to re-oxidize the partially reduced ceria ($\text{CeO}_{2-\delta}$), thus completing the cycle. In this second step, the parent CeO_2 was regenerated by consuming oxygen from CO_2 , along with the production of additional CO. The reaction rates values were obtained from the slopes of O and CO evolution profiles by performing linear regression.

The observed variations in reaction rates as a function of temperature and partial pressure are given in Figure 3. The rate of reduction was found to be influenced by the temperature (Figure 3a). On the contrary, the effect of temperature on the CO_2 -induced re-oxidation rate was found to be much lower. In addition, the effect of partial pressure

(concentration) of the gaseous reactant (CH_4 for reduction and CO_2 for oxidation) on the conversion was monitored (Figure 3b). In this case, both the rates of reduction and re-oxidation were found to be influenced by the partial pressures of CH_4 and CO_2 , respectively. The logarithm plot of these rates variations (assuming $r = k \cdot (p_{\text{CH}_4 \text{ or } \text{CO}_2})^n$, where p denotes the partial pressure of CH_4 or CO_2) against inverse temperature and reactant gas concentration allowed for the determination of the activation energies and reaction orders ($E_a = 109 \text{ kJ} \cdot \text{mol}^{-1}$ for CH_4 -induced reduction and $36 \text{ kJ} \cdot \text{mol}^{-1}$ for CO_2 -induced re-oxidation, and reaction orders $n = 0.62$ and 0.53 with respect to CH_4 and CO_2 , respectively) [21].

Figure 3. Variation in reaction rates as a function of (a) temperature and (b) reactant concentration.

In solid-state kinetics, mechanistic interpretations usually involve the identification of a reasonable reaction model, because accurate information about individual reaction steps is often difficult to obtain. A model, in general, is a mathematical representation of experimental observations. Mechanistic considerations enable kinetic models to be categorized as reaction order, nucleation, shrinking core, or diffusion-controlled models. Solid-state conversion profiles for CeO_2 oxygen carriers were obtained from the experimental mass variations using Equation (10) and are displayed as a function of time in Figure 4. Preliminary information regarding the reaction mechanism can be obtained from the graphical method developed by Hancock and Sharp [41].

Figure 4. Experimental solid-state conversion profiles as a function of time (a) at selected temperatures during reduction and (b) at selected temperatures during re-oxidation, (c) effect of CH₄ partial pressure during reduction, and (d) effect of CO₂ partial pressure during re-oxidation. The partial pressure of the reactant gases was kept at 40% in (a,b). Experiments with varying partial pressures in (c,d) were carried out at 1000 °C.

Accordingly, the relationship between solid-state conversion and time can be expressed as:

$$\ln(-\ln(1-X_i)) = m \ln(t) + \ln(\alpha) \quad (3)$$

where m is a constant representing the reaction mechanism and dimensionality, and α is a constant representing the growth rate. If the solid conversion range is limited to values ranging from 0.15 to 0.5, the kinetics is not affected by the experimental uncertainties and errors during the initial and final phases of the reaction. Depending on the values of m , an approximate reaction mechanism may be assigned.

As shown in Figure 5, representing a plot of $\ln(-\ln(1-X_i))$ vs. $\ln(t)$, a linear relationship was clearly observed at each studied temperature for CeO₂ reduction, with m values close to 1 (0.91 to 1) regardless of temperatures. For CO₂-induced re-oxidation, a linear relationship was also observed with m values ranging between 1.49 and 1.57. Specific m values were previously assigned by various authors to determine appropriate models indicating whether the reaction is diffusion-controlled or phase boundary-controlled [42–44]. For instance, when the m values are below 1, the mechanism is diffusion-controlled. In general, diffusion models of varying order exhibit m values between 0.5 and 0.6. When the m values are higher than unity, a phase boundary-controlled mechanism is expected. However, it should be noted that identifying a reaction mechanism solely on the basis of Hancock and Sharp plots can be erroneous, as reported previously [45,46]. Besides, different models of varying orders exist for similar m values. Thus, a more realistic model fitting approach was used in this study by comparing several classic kinetic models to fit the experimental data obtained using the solar reactor. All these models were screened for CH₄-induced reduction and CO₂-induced re-oxidation of CeO_{2-δ}. The experimental values of solid-state conversions ranging from $X_i = 0.1$ to 0.9 were used in order to incorporate significant values of conversion in the considered data range and, at the same time, to avoid experimental artefacts and errors [34,41].

Figure 5. Hancock and Sharp plots for experimental solid-state conversion data at selected temperatures during (a) reduction and (b) re-oxidation.

Initially, the first-order model (F1) was used to fit the experimentally obtained solid-state conversion data for CH_4 -induced reduction. In this case, it is assumed that the reaction occurs in the oxygen carrier throughout the particles and the mass of the oxygen carrier grain due to oxygen release/uptake varies linearly during the reactions [47,48]. However, from the values of regression coefficient (R^2), sufficient correlations were not observed between the experimental and model data, as reported in the Supplementary Materials (Figure S1). In a similar manner, extremely poor correlations were observed for the experimental conversion data in the case of the power law model (PLM) and 3D Janders (D3) and Ginstling (D4) diffusion models [32–37]. The obtained regression plots are reported in the Supplementary Materials (Figures S2–S4, respectively). In contrast, both the shrinking core model (SCM) and nucleation and nuclei growth model (NGM) were found to exhibit superior agreement with the experimental conversion data. Therefore, 2D and 3D variants of SCM designated as R2 and R3, as well as 2D and 3D variants of NGM designated as AE2 and AE3, were explored to further elucidate the redox kinetic information.

In SCM, a spherical particle is gradually modified as a result of the reaction occurring on the external surface during the course of the reaction [32–37]. In this case, the surface chemical reaction can be considered as rate-limiting, and can be expressed in 2D (R2) as:

$$gX_i = [1 - (1 - X_i)^{1/2}] = kt \quad (4)$$

For the 3D SCM (R3) reaction, Equation (4) transforms into:

$$gX_i = [1 - (1 - X_i)^{1/3}] = kt \quad (5)$$

Two-dimensional SCM (R2), assuming a contracting cylinder mechanism, exhibited excellent correlation with the experimental conversion data obtained at different temperatures (900, 1000, and 1050 °C) for the reduction of CeO_2 in the presence of CH_4 with R^2 values greater than 0.99. The values of R^2 decreased slightly (~ 0.98) for the plots obtained in the case of re-oxidation under CO_2 and for the plots obtained by varying the partial pressures of gaseous reactants. The obtained reaction profiles are shown in Figure 6. In the case of 3D SCM (R3), assuming a contracting sphere mechanism, R^2 values in some cases decreased to ~ 0.97 , and the corresponding figures are shown in the Supplementary Materials (Figure S5).

Figure 6. Comparison of experimental conversion data with 2D SCM (R^2) predictions for CeO_2 during (a) CH_4 -induced reduction at selected temperatures, (b) CO_2 -induced re-oxidation at selected temperatures, (c) varying CH_4 partial pressure during reduction, and (d) varying CO_2 partial pressure during re-oxidation. The partial pressure of the reactant gases was kept at 40% in (a,b). Experiments with varying partial pressures in (c,d) were carried out at 1000 °C.

For NGM, the gas–solid reaction proceeds via the formation of nuclei followed by subsequent growth [32–37]. Activation of the first nuclei takes place during the induction period, and the reaction rate increases with the number of nuclei during this period. The gX_i function is then expressed as:

$$gX_i = [-\ln(1 - X_i)]^{(n-1)/n} = kt \quad (6)$$

where n is the Avrami exponent, indicative of the reaction mechanism and growth dimension. Thus, the random nucleation model (RNM) resulting from a value of $n = 1$ simplifies into the first-order model (F1), in which an induction period is not present. The obtained results are summarized above and are shown in the Supplementary Materials (Figure S1). Two-dimensional or three-dimensional nuclei growth is assumed for $n = 2$ or 3, respectively, and the corresponding gX_i functions can be represented by the following equations.

$$gX_i = [-\ln(1 - X_i)]^{1/2} = kt \quad (7)$$

$$gX_i = [-\ln(1 - X_i)]^{2/3} = kt \quad (8)$$

Two-dimensional NGM (AE2) exhibited an excellent correlation with the experimental conversion data obtained at different temperatures (900, 1000, and 1050/1070 °C) and gaseous reactant partial pressures for CeO_2 reduction and re-oxidation. The values of the correlation coefficient (R^2) remained greater than 0.99 in all these cases. The corresponding plots are shown in Figure 7. The R^2 values decreased slightly to ~0.98, when 3D NGM (AE3) was used, and the obtained plots are shown in the Supplementary Materials (Figure S6). As variants (2D and 3D) of SCM and NGM were found to exhibit the best correlations with the experimental reduction and re-oxidation data of CeO_2 oxygen carriers, the values of kinetic rates (k) in each case were obtained from the slopes of the plots by performing linear regression. The corresponding values obtained at different temperatures during reduction and re-oxidation were used for determining the pre-exponential factor (A) and activation energy (E_a), from the Arrhenius plot (Figure 8).

Figure 7. Comparison of experimental conversion data with 2D NGM (AE2) predictions for CeO_2 during (a) CH_4 -induced reduction at selected temperatures, (b) CO_2 -induced re-oxidation at selected temperatures, (c) varying CH_4 partial pressure during reduction, and (d) varying CO_2 partial pressure during re-oxidation. The partial pressure of the reactant gases was kept at 40% in (a,b). Experiments with varying partial pressures in (c,d) were carried out at 1000 °C.

Figure 8. Arrhenius plots for (a) CH_4 -induced reduction and (b) CO_2 -induced re-oxidation over CeO_2 oxygen carrier performed in solar thermogravimetric reactor using concentrated solar energy.

The obtained values of E_a and A are compiled in Table 1. Significant differences were not observed in the values of activation energies obtained using the different kinetic models. However, the activation energy for the CH_4 -induced reduction of CeO_2 remained much higher than that observed for CO_2 -induced re-oxidation. In comparison with previous results for thermal reduction, the present values were found to be lower. It is to be noted that because of the variations in material composition, experimental parameters, and kinetic models used in different studies, a comparison with previously reported values will not be precise.

Table 1. Kinetic parameters obtained from various mechanistic functions for CH₄-induced reduction and CO₂-induced re-oxidation over CeO₂ oxygen carrier in a solar thermal reactor.

Reaction Model	T (°C)	Rate Constant (s ⁻¹)		Ea (kJ·mol ⁻¹) ^a		A (s ⁻¹) ^b	
		Reduction	Re-Oxidation	Reduction	Re-Oxidation	Reduction	Re-Oxidation
2D NGM	900	1.9×10^{-3}	2.7×10^{-3}	79.61	10.5	6.69	127.0
	1000	3.6×10^{-3}	2.9×10^{-3}				
	1050/1070	4.8×10^{-3}	3.1×10^{-3}				
3D NGM	900	2.4×10^{-3}	3.5×10^{-3}	80.28	8.2	9.07	123.6
	1000	4.6×10^{-3}	3.7×10^{-3}				
	1050/1070	6.1×10^{-3}	3.9×10^{-3}				
2D SCM	900	1.1×10^{-3}	1.5×10^{-3}	76.68	9.5	2.86	252.9
	1000	2.0×10^{-3}	1.6×10^{-3}				
	1050/1070	2.7×10^{-3}	1.7×10^{-3}				
3D SCM	900	8.0×10^{-4}	1.2×10^{-3}	83.49	11.7	4.21	252.3
	1000	1.6×10^{-3}	1.3×10^{-3}				
	1050/1070	2.1×10^{-3}	1.4×10^{-3}				

^a Activation energy; ^b Pre-exponential factor.

In general, the values of Ea for the CH₄-induced reduction obtained in this study are consistently lower than those obtained for the purely thermal reduction of CeO₂ [21]. This can be due to the fact that the presence of CH₄ as a reducing agent better facilitates the reduction reaction. In addition, the values of activation energies of reduction are in close agreement with previous results, using similar composition and reaction conditions. However, the Ea values obtained in the present study for CO₂-induced re-oxidation seem to be lower [21,28]. In contrast, pre-exponential factors (A) were found to follow the opposite trend, exhibiting higher values for the re-oxidation reaction. Moreover, the values of pre-exponential factors were found to vary significantly from the reported ones and to be influenced by the model used. Considering the better-quality fits observed for the entire range of temperatures and gaseous reactant concentrations, the 2D NGM (R2) most suitably represents the redox reactions of CeO₂ oxygen carriers under the conditions considered in this study. In general, the nucleation and nuclei growth model assumes that the formation of a new reactive phase is crucial for the progress of the reaction. The reaction rate will depend on the number of this new reactive product nuclei (CeO_{2-δ} in the present study) distributed randomly across the solid CeO₂ material. Growth of the nuclei in a 2D scheme will take place, followed by the simultaneous formation of new nuclei until they overlap, causing nucleation. Further, the growth of grains throughout the parent CeO₂ surface will take place until the transformation is completed. Equation (7) describes the process of nucleation and crystal growth on a phase boundary surface formed between the parent oxide and a uniform distribution of the newly formed product nuclei. A thicker product layer is formed gradually on the parent CeO₂ surface. Consumption of the released oxygen from the CeO₂ oxygen carrier to form the partially reduced state (CeO_{2-δ}) during the course of the reaction and the associated structural changes may probably result in the formation of some extent of porosity, which can enhance the reaction between the oxygen carrier and CH₄, by promoting the diffusion of gaseous components. The termination of nuclei growth can take place by the overlap of grain boundaries. As re-oxidation data also agree well with 2D NGM (R2) in this study, the reverse formation of CeO₂ from CeO_{2-δ} will proceed during CO₂-induced re-oxidation in the same manner as explained above.

3. Experimental

3.1. Material Preparation

Commercial CeO₂ was used as received from Aldrich (<5 μm, 99.9% purity) without any further chemical treatments. To warrant their structural stability, an appropriate amount of the material was calcined for 2 h under air at 1000 °C before performing the solar experiments. This thermal pre-treatment also ensures the removal of undesired impurities, including moisture that was adsorbed on the surface of the oxygen carrier. The

material after pre-treatment was cooled down to ambient temperature and was immediately used for redox cycling experiments.

3.2. Characterization of Materials

Structural and morphological characterizations of CeO_2 before and after redox cycles were carried out. X-ray diffraction (XRD) patterns were obtained with the Cu $K\alpha$ radiation (0.15418 nm, angular range 20–80 2θ , steps 0.02 2θ , recording time of 2 s) using a Philips PW 1820 diffractometer (Amsterdam, The Netherlands). The identification of the crystalline phase was performed by comparing the diffractograms with standard diffraction patterns of reference compounds (powder diffraction file PDF-2, International Centre for Diffraction Data, ICDD). The materials recovered after cycling experiments were mixed in a mortar before XRD analysis. The particle morphology and surface microstructure characterizations were performed by high-resolution field emission scanning electron microscopy (FE-SEM, Hitachi S4800, Tokyo, Japan).

3.3. Redox Experiments

Thermochemical redox reactions were carried out on an experimental setup previously developed in PROMES-CNRS (France), for investigating thermochemical solid–gas reactions under controlled reaction atmospheres [29]. A schematic representation of the tubular solar thermogravimetric reactor is provided in Figure 9. Concentrated solar energy is used to provide the process energy for both reduction and re-oxidation reactions. The process heat at high temperature is supplied to the reactor by using a horizontal-axis solar furnace. It consists of a sun-tracking heliostat that reflects the incident solar irradiation towards a 2 m-diameter parabolic dish concentrator (delivering a Gaussian concentrated solar flux distribution at the focal plane with a maximum peak flux density of 16 MW/m^2 for a direct normal irradiation DNI of 1 kW/m^2). The solar thermogravimetric reactor includes a cavity-type receiver. At the cavity front, the 15 mm-diameter aperture is positioned at the focal point of the solar concentrator (0.85 m ahead from the concentrator) for favoring the optimum access and the absorption of concentrated solar radiation within the cavity-receiver, while alleviating re-radiation losses toward the cavity outside. The cavity is made of high-temperature-resistant graphite walls, and the surroundings of the walls are lined with a ceramic insulation layer. The inside of the reactor (cavity) is separated from the outside atmosphere by a transparent Pyrex glass window at the front. Regarding the solar-driven thermogravimetric measurements, an appropriate amount (~ 1 g) of the oxygen carrier to be analyzed was placed as a loose packed-bed in an alumina crucible (12 mm i.d., 15 mm o.d., 10 mm height) that was connected to a micro-balance (Mettler Toledo, Columbus, OH, USA, weighting module, 0.01 mg readability) thanks to a vertical alumina rod. The sample and holder were settled inside a cylindrical lining tube made of alumina (25 mm o.d., 20 mm i.d.), and were in stable equilibrium at the center of the tube. The reactive gas flow was injected in the upward direction and reacted with the oxide bed sample when reaching the crucible. The temperature during redox cycles was measured just above the reacting sample by using a B-type thermocouple placed inside the alumina tube. This measurement corresponds to the reaction temperature because a homogeneous temperature distribution is provided in the reacting zone thanks to the cavity-type solar reactor configuration. Thus, the zone where the sample holder is placed inside the absorber tube can be considered isothermal. The heating of the sample mainly occurs via radiative heat transfer from the nearby surrounding hot walls of the alumina tube. Prevailing heat transfer is mainly radiative due to the high temperatures in this zone, and a thermal radiative equilibrium is established inside the black-body cavity. Moreover, the extremely limited size of the crucible and its position at the center of the heated zone warrant the absence of a temperature gradient in the crucible and inside the reacting powder bed. The flow-rates of purge carrier gas (Ar, 99.999% purity, with O_2 volume content < 2 ppm(v)), methane (CH_4 , 99.95% purity), and carbon dioxide (CO_2 , 99.995% purity) were controlled and regulated by using electronic mass-flow controllers (Brooks, Hatfield, PA, USA). The

total gas flow-rate was kept constant (at $0.5 \text{ L} \cdot \text{min}^{-1}$) to maintain constant the gas/solid contact time in the tube.

Figure 9. Schematic representation of the solar thermogravimetric reactor equipped with a parabolic dish concentrator, used for carrying out the thermochemical redox cycles over CeO_2 oxygen carrier.

The CeO_2 oxygen carrier was placed in the solar reactor under a constant flow of Ar ($0.5 \text{ L} \cdot \text{min}^{-1}$). After reaching the desired temperature (900, 1000, and 1050/1070 $^{\circ}\text{C}$), a continuous flow of CH_4 (for reduction) or CO_2 (for re-oxidation) was introduced to attain a reactant mole fraction of 20, 40, or 60%, until the oxygen release/uptake from the CeO_2 oxygen carrier was complete. The amount of oxygen evolved (δ) was calculated according to the equation,

$$\delta = (\Delta m / m) \times (M_{\text{CeO}_2} / M_{\text{O}}) \quad (9)$$

where Δm is the total mass loss during reduction (or mass gain during re-oxidation), m is the initial amount of the material used for redox experiments, M_{CeO_2} is the molar mass of CeO_2 , and M_{O} is the molar mass of an oxygen atom. The same equation (Equation (9)) was used for calculating the evolved CO amount by just replacing the mass loss with the mass gain during re-oxidation. δ thus quantifies the amount of either O or CO evolved (in $\text{mol} \cdot \text{mol}^{-1}$).

3.4. Kinetic Data Processing

Reduction and re-oxidation kinetics of CeO_2 oxygen carriers are strongly desired for the rational design and optimization of solar thermochemical reactors. Predicting intrinsic reaction parameters that reflect the overall reaction mechanism is challenging. Indeed, detailed mechanisms and steps involved in the oxygen release (reduction) and uptake (oxidation) of CeO_2 are often difficult to obtain experimentally. On the other hand, a systematic screening of a series of reaction models to select the most appropriate one based on the available experimental data can be a promising avenue to unravel the reaction kinetics. Reduction and re-oxidation isothermal reactions were carried out at selected temperatures (900, 1000, and 1050/1070 $^{\circ}\text{C}$) to obtain the O_2 evolution (release or uptake) profiles against time. The solid material conversion fractions were then obtained from Equation (10), where X_i denotes the extent of conversion during reduction or re-oxidation, as appropriate.

$$X_i = (\Delta m_t / \Delta m) \quad (10)$$

where Δm_t is the mass loss during reduction (or gain during re-oxidation) at a specific time and Δm is the total mass variation during the reaction. This metric was further used to determine the reaction kinetics for the fresh particles. The intrinsic kinetics of the gas–solid reaction can be formulated considering an overall reaction rate being a function of the extent of reduction/re-oxidation of solid material ($f(X_i)$) and the gas-phase composition ($f(G)$), as represented by the following equation.

$$dX_i/dt = k \times fX_i \times fG \quad (11)$$

where k is the temperature-dependent overall rate constant of the reaction. The fG function in Equation (11) can be considered as a single pseudo-constant provided the reactions were carried out at the same feed flow-rate and reactant partial pressure [36]. Thus, Equation (11) can be simplified to:

$$dX_i/dt = k \times fX_i \quad (12)$$

By integrating Equation (12) under isothermal conditions, the integral form (gX_i) of the reaction model is obtained and can be expressed as:

$$gX_i = \int_0^x \left(\frac{dX_i}{fX_i} \right) \quad (13)$$

In the present study, solid-state kinetic models exhibiting the best correlation with the experimental data were utilized for identifying the kinetic parameters and reaction mechanism. The rate constants (k) thus calculated from the slope for different temperatures were then expressed as a function of temperature via the following Arrhenius equation.

$$k = A \cdot \exp(-E_a/RT) \quad (14)$$

where E_a is the activation energy (in $\text{kJ} \cdot \text{mol}^{-1}$) and A is the pre-exponential factor (in s^{-1}). The method for model fitting to the experimental data is based on the determination of gX_i linearity with time. The linear fit provides a slope that represents the reaction rate constant (k). The evaluation of the kinetic parameters, including the pre-exponential factor (A) and apparent activation energy (E_a), can be achieved by determining the reaction rate constant at different temperatures. Then, both the E_a and A values can be calculated based on the resultant logarithm plot of the Arrhenius expression (Equation (14)) from the slope and intercept, respectively.

4. Conclusions

Fluorite-structured nonstoichiometric CeO_2 represents the most promising and benchmark oxygen carrier for solar-driven thermochemical fuel production. In this study, the solid-state redox kinetics of CeO_2 during both isothermal CH_4 -induced reduction and CO_2 -induced re-oxidation were investigated. Such a coupling of CH_4 partial oxidation with CO_2 splitting can produce syngas, which is an important feedstock for various industrial processes. The reactions were carried out using concentrated solar energy in a customized solar thermogravimetric reactor designed for carrying out thermochemical reactions under controlled atmospheres. Different classical solid-state kinetic models were utilized to derive the mechanism for CeO_2 redox reactions in the solar thermal reactor. Both 2D and 3D variants of the shrinking core model (SCM) and nucleation and nuclei growth model (NGM) were found to exhibit the best correlation between the experimental data and model predictions. The values of apparent activation energies ($\sim 80 \text{ kJ} \cdot \text{mol}^{-1}$ for reduction and $\sim 10 \text{ kJ} \cdot \text{mol}^{-1}$ for re-oxidation) and pre-exponential factors ($\sim 2\text{--}9 \text{ s}^{-1}$ for reduction and $\sim 123\text{--}253 \text{ s}^{-1}$ for re-oxidation) were obtained. The observed disparities in the kinetic parameters in comparison with those available in the literature can be attributed to the variations in reaction conditions, solar reactor configuration, and kinetic models used. As superior correlations were observed for 2D NGM (R2) throughout the conditions

used in this study, this model most appropriately depicts the redox reaction mechanism of CeO₂ oxygen carrier in the solar thermal reactor.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11060723/s1>, Figures S1–S6 include additional information regarding the comparison between experimental conversion data with solid-state reaction models.

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Nomenclature

δ	Amount of O or CO evolved during reduction or oxidation ($\text{mol} \cdot \text{mol}^{-1}$)
A	Pre-exponential factor (s^{-1})
E _a	Activation energy ($\text{kJ} \cdot \text{mol}^{-1}$)
k	Temperature-dependent overall rate constant of the reaction (s^{-1})
M _{CeO₂}	Molar mass of CeO ₂ ($\text{kg} \cdot \text{mol}^{-1}$)
M _O	Molar mass of oxygen atom ($\text{kg} \cdot \text{mol}^{-1}$)
m	Initial amount of the material (kg)
Δm_t	Mass loss during reduction (or gain during re-oxidation) at a specific time (kg)
Δm	Total mass variation during the reaction (kg)
n	Avrami exponent indicative of the reaction mechanism and growth dimension
t	time (s)
X _i	Extent of conversion

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