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Solid-state Re-oxidation Kinetics of A/B-site Substituted LaMnO₃ during Solar Thermochemical CO₂ Conversion

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Abstract. Perovskite oxides exhibit noteworthy performance as efficient oxygen carriers for carrying out the two-step thermochemical conversion of CO₂ using concentrated solar energy (CSE). In the present study, the effect of composition on the solid-state re-oxidation kinetics of La_{0.5}Sr_{0.5}MnO₃ and LaCo_{0.5}Mn_{0.5}O₃ oxygen carriers is investigated. Thermochemical CO₂ splitting reactions are carried out at several selected temperatures and a series of kinetic models are explored for deducing the reaction mechanisms. Results indicate that the most suitable model describing the re-oxidation mechanism depends on the oxygen carrier. A two-step reaction mechanism is observed for La_{0.5}Sr_{0.5}MnO₃ (first order model and 2D shrinking core model) depending on the extent of conversion whereas a diffusion controlled (3D-Ginstling) mechanism is identified for LaCo_{0.5}Mn_{0.5}O₃. The values of apparent activation energies (E_a) are remarkably low (~ 5 kJ.mol⁻¹) and even negative, indicating an “anti-Arrhenius” behavior. Pre-exponential factors (A) are found to be low and influenced by the model used. Enthalpies of activation ($\Delta H^\ddagger = -6$ to -18 kJ.mol⁻¹) depend on the extent of conversion and composition, whereas entropies of activation ($\Delta S^\ddagger = -0.33$ kJ.K⁻¹mol⁻¹) remained constant. The observed discrepancies in the re-oxidation mechanism can probably be attributed to thermal stability aspects, variations in lattice functionalities during the reaction, undesired side reactions or a combination of these effects.

1. Introduction

Solar energy is the most abundant form of energy that can possibly replace the fossil derived energy scenario. However, solar energy is intermittent and therefore needs to be captured and stored for long term use without disruption. Utilization of concentrated solar energy (CSE) for providing process heat for thermochemical conversion of CO₂ into CO seems to be promising on this regard.^[1-4] In this case, the entire solar energy spectrum can be effectively converted and at the same time a greenhouse gas gets converted into an industrially relevant feedstock. Moreover, this strategy of storing solar energy in chemical bonds in the form of transportable fuels is compatible with the existing storage and transport infrastructure. In general, solar thermochemical routes are composed of two steps. First, the high temperature partial reduction of the oxygen carrier accompanying the evolution of oxygen would take place. In the second step, the partially reduced metal oxide would be re-oxidized into its original form in presence of an oxidant (*e.g.*, CO₂) at comparatively lower temperatures.^[5] CeO₂ is the most widely studied non-stoichiometric oxygen carrier for solar thermochemical fuel production so far. However, high reduction temperatures inherent to the case of CeO₂ forced the scientific community to look for other alternatives.^[1,4]

Among the alternative materials, perovskite structured mixed metal oxides (ABO₃) are the most extensively studied.^[2,3,6] These materials can conveniently accommodate a wide range of A and B-site cations in their crystal lattice. Thus, the physicochemical properties and redox chemistry of these materials can be tailored to a large extent. Studies so far indicate La_{0.5}Sr_{0.5}MnO₃ as the one of the most promising oxygen carriers among perovskites.^[7-10] However, owing to the structural and compositional flexibility of these materials, further breakthroughs can be expected in the near future. While CeO₂ based oxygen carriers favor the re-oxidation reaction, perovskites on the other hand favor reduction. Therefore, strategies to enhance the re-oxidation efficiency in these latter materials are well sought and the key to this may be hidden in an in-depth understanding of the mechanistic functioning of these materials.

Also, from an engineering perspective, the reaction kinetics of these materials are important for rational solar reactor design and modification purposes. A few investigations dealing with reduction reaction kinetics were performed by various authors.^[11-14] However, synthesis parameters (reagents, calcination, etc) can change the surface and redox properties of perovskites to some extent and such variations will obviously be reflected in their applications. Also, experimental conditions used by various authors for carrying out the solar thermal processes differ significantly. For example, most of the studies detailing the solid-state re-oxidation kinetics of perovskites employ O₂ as the oxidant (as in chemical looping combustion).^[12,15,16] In order to overcome such limitations, comparisons are to be made with consistent material aspects and reaction conditions.

In the present study, the effect of perovskite oxygen carrier composition on the solid-state thermochemical re-oxidation kinetics in presence of CO₂ is investigated. Two promising candidates (La_{0.5}Sr_{0.5}MnO₃ and LaCo_{0.5}Mn_{0.5}O₃) in terms of CO₂ splitting efficiency and stability are chosen for the purpose. La_{0.5}Sr_{0.5}MnO₃ (LSM) is widely considered as the most promising perovskite oxide for solar thermal applications and is therefore selected as an A-site substituted candidate.^[7-9,17,18] Similarly, LaCo_{0.5}Mn_{0.5}O₃ (LCM) is one promising B-Site substituted perovskite oxide for solar thermochemical fuel production.^[10] For both materials, a thermal reduction was carried out at 1400 °C. Then, the amount of oxygen uptake during CO₂ induced re-oxidation was monitored continuously. For LSM, models based on phase boundary control were found to exhibit good correlation with the experimental data. On the other hand, for LCM, diffusion control was dominant during re-oxidation. The activation parameters including activation energy (E_a), pre-exponential factor (A), activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) were determined using appropriate methods and discussed

2. Results and Discussion

Two oxygen carriers with perovskite structure were chosen in this study to elucidate the mechanism of solid-state re-oxidation in solar thermochemical CO₂ conversion. Crystallinity, phase purity and composition are the crucial factors playing a decisive role in determining the redox chemistry of oxygen carriers. Primarily, the synthesized oxygen carriers were analyzed by powder X-ray diffraction (XRD). Intense reflection peaks corresponding to the perovskite structure were observed in the wide-angle region of the XRD patterns. Minor shifts in peak positions were observed in accordance with the composition of the oxygen carrier. Lattice substitutions in complex oxides can sometimes result in cation segregation leading to the formation of undesired phases. For the materials used in this study, peaks corresponding to such binary oxide impurities were not present in the XRD pattern. These observations are in agreement with previous results.^[17,18] In short, the synthetic parameters used were suitable for producing phase pure materials of the selected oxygen carriers. The obtained diffraction patterns are shown in **Figure 1**.

Figure 1. Wide angle powder XRD patterns of as-synthesized La_{0.5}Sr_{0.5}MnO₃ (LSM) and LaCo_{0.5}Mn_{0.5}O₃ (LCM) oxygen carriers calcined at 1400 °C and 1500 °C, respectively.

Further information regarding surface structure and morphology were obtained from the SEM images. Irrespective of the composition, the perovskite oxygen carriers displayed the formation of crystalline and dense predominantly micrometer sized particles (3-5 μm) with uneven morphologies and agglomerated forming random network structures. Significant variations in grain sizes with respect to the variation in the composition were not observed in

the SEM images. Therefore, the surface morphology and structural properties of these oxygen carriers were little influenced by the synthesis method or composition. Representative SEM images are provided in **Figure 2**.

Figure 2. Representative SEM images of as-synthesized $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSM) and $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LCM) oxygen carriers calcined at 1400 °C and 1500 °C, respectively.

The re-oxidation performance of the two perovskite oxygen carriers was analyzed separately.

The initial thermal reduction step was carried out at a fixed temperature of 1400 °C. Previous studies indicated that at this temperature, maximum amount of oxygen release is facilitated in most of the perovskite oxides while ensuring a minimum extent of sintering.^[10] The partially

reduced perovskites formed after reduction, were individually subjected to re-oxidation in

presence of CO_2 and the obtained mass variation profiles are shown in **Supporting**

Information Figure S1. Temperatures and reaction durations for this CO_2 induced re-

oxidation process were based on the oxygen carrier composition so as to ensure maximum

performance while minimizing the stability concerns. The resulting CO evolution profiles as a

function of time calculated from the experimental mass variations using Equation (2), are

shown in **Figure 3a and b**. For $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSM), the evolution of CO was found to be

dependent on temperature with maximum value observed at 1200 °C and minimum at 900 °C

(Figure 3a). On the contrary, significant variation in CO evolution was not observed for

$\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LCM), under the studied temperatures. The values obtained for both of these oxygen carriers are compiled in **Table 1** and **Supporting Information Table S1**. From the experimental mass variations determined during re-oxidation reactions, the solid-state conversion profiles as a function of time were also deduced for the two oxygen carriers (Figure 3c and d). This information was utilized for further elucidating the solid-state kinetic mechanism.

Figure 3. Experimental CO evolution profiles as a function of time at selected temperatures during re-oxidation of (a) $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSM) and (b) $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LCM) oxygen carriers. The corresponding solid-state conversion profiles are shown in (c) and (d).

A model-free approach developed by Hancock and Sharp can be used to obtain preliminary information regarding the mechanism of redox reactions.^[19] Accordingly, if the range of solid conversion is limited between 0.15 to 0.5, the values of m and α (slope and intercept respectively) obtained from a plot of $\ln[-\ln(1-X_i)]$ against $\ln(t)$, can be used to assume an approximate reaction mechanism.^[19,20-22] For instance, when the values of m are below 1, the mechanism is predominantly diffusion controlled whereas a phase boundary control is expected for m values higher than unity. In the present study, the plot of $\ln[-\ln(1-X_i)]$ against $\ln(t)$ (**Figure 4**), indicated a linear relationship for all the studied temperatures for both

perovskites. The values of slopes (m) are provided in Table 1. For LSM, m values were closer to unity (0.99 to 1.07) and for LCM, the values ranged from 1.22 to 1.34.

Table 1. Maximum amounts of CO evolved during re-oxidation under CO₂ (inlet concentration 50%) and temperatures used for carrying out the reactions. m values represent the slopes obtained from the linear regression of Hancock and Sharp plots.

Oxygen carrier	T [°C]	CO evolved [$\mu\text{mol.g}^{-1}$]	m
La _{0.5} Sr _{0.5} MnO ₃ (LSM)	900	185	1.07
	1050	236	1.08
	1200	243	0.99
LaCo _{0.5} Mn _{0.5} O ₃ (LCM)	900	181	1.27
	1000	286	1.34
	1100	281	1.22

Figure 4. Hancock and Sharp plots for experimental solid-state conversion data at selected temperatures during CO₂ induced re-oxidation over (a) La_{0.5}Sr_{0.5}MnO₃ (LSM) and (b) LaCo_{0.5}Mn_{0.5}O₃ (LCM) oxygen carriers.

It should be noted here that in many cases it is extremely difficult to identify the reaction mechanism solely on the basis of Hancock and Sharp plots.^[23,24] For instance, different models of varying orders exist for similar values of m . Moreover, this method can hardly detect the presence of complicated multi-step reaction mechanisms. On the other hand, model fitting approach can provide detailed insights and hence this method was used to draw more realistic conclusions regarding the re-oxidation reaction of perovskites. Accordingly, several classical kinetic models were screened for CO₂ induced re-oxidation of LSM and LCM. The values of solid-state conversions between $X_i = 0.1$ and $X_i = 0.9$, were initially used for the purpose to ensure that data range incorporates significant extents of conversion and also to avoid experimental artefacts and errors.^[13,19]

Figure 5. Comparison of experimental conversion data ($X_i = 0.1 - 0.9$) with model predictions for CO₂ induced re-oxidation of La_{0.5}Sr_{0.5}MnO₃ (LSM) oxygen carrier at selected temperatures. (a) 2D nucleation and nuclei growth model (AE2), (b) 3D nucleation and nuclei growth model (AE3), (c) 2D shrinking core model (R2) and (d) 3D shrinking core model (R3). Preliminary observations indicate that 2D nucleation and nuclei growth model, also called Avrami-Erofe'ev model (AE2), 3D nucleation and nuclei growth model (AE3), 2D shrinking

core model (R2) and 3D shrinking core model (R3) were exhibiting superior correlations with the experimental conversion data for LSM. Other models exhibiting lower correlation with experimental data are provided in **Supporting Information Figure S2**.

Nucleation and nuclei growth models (NGM) assume the formation of a product nuclei, followed by subsequent growth, with the reaction rate proportional to the number of this newly formed nuclei.^[12-14,25-27] Growth of the nuclei and formation of new nuclei will take place simultaneously until they overlap causing nucleation. Following the nucleation event, the grains grow throughout the surface until the transformation is completed. The gXi function can be expressed as:

$$gXi = [-\ln(1-Xi)^{(n-1)/n}] = kt \quad (1)$$

where n is the Avrami exponent indicative of the reaction mechanism and growth dimension. For 2D and 3D nuclei growth, n assumes the values of 2 and 3, respectively. Accordingly, Equation (1) transforms into:

$$gXi = [-\ln(1-Xi)^{(1/2)}] = kt \quad (2)$$

$$gXi = [-\ln(1-Xi)^{(2/3)}] = kt \quad (3)$$

Shrinking core model (SCM) assumes that the reaction occurs on the external surface of the particle, undergoing gradual changes during the course of the reaction.^[12-14,25-27] Here, the surface chemical reaction is considered as rate-limiting. 2D variant assumes a contracting cylinder mechanism as expressed in Equation (4) and 3D variant assumes a contracting sphere mechanism as expressed in Equation (5):

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

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

In all these cases, the obtained values of regression coefficients (R^2) were higher than 0.995 at all the re-oxidation temperatures. The resulting profiles indicating the correlation between experimental conversions and model predictions are provided in **Figure 5**. Surprisingly, the values of rate constants (**Supporting Information Table S2**) derived from the slopes of

aforementioned reaction models were not found to vary in accordance with the temperature, as per Arrhenius theory (Equation 18). This phenomenon clearly indicates that the CO₂ induced re-oxidation of LSM is not a straightforward representation of any of the models mentioned above. One alternative possibility is that the reaction is following a multi-step mechanism.

Figure 6. Comparison of experimental conversion data ($X_i = 0.05 - 0.6$) with model predictions for CO₂ induced re-oxidation of La_{0.5}Sr_{0.5}MnO₃ (LSM) oxygen carrier at selected temperatures. (a) First order model (F1), (b) 2D shrinking core model (R2), (c) 3D shrinking core model (R3), and (d) 3D nucleation and nuclei growth model (AE3).

Therefore, the experimental data points obtained for solid-state conversions were randomly split into several regions and screening was carried out. It was observed that a two-step mechanism is necessary to describe the behavior of LSM. For the solid-state conversion (X_i) between 0.05 to 0.60, first order model (F1), 2D SCM (R2), 3D SCM (R3) and 3D NGM (AE3) were found to define the re-oxidation mechanism in the most appropriate manner. Among these, the best fit between the experimental data and the model predictions were observed for F1 with $R^2 \sim 0.999$ for all the temperatures. The corresponding profiles detailing

the correlation between experimental conversions and model predictions are provided in **Figure 6**.

First order model (F1) assumes that the reaction occurs throughout the particles of the oxygen carrier and the mass of the oxygen carrier grain changes linearly during the reaction as a result of oxygen release/uptake.^[28,29] In other words, when the value of Avrami exponent becomes unity ($n = 1$), the nucleation and nuclei growth model (NGM) simplifies into first order model (F1), where the nuclei growth takes place randomly. The gXi function in this case can be expressed as:

$$gXi = -\ln(1 - Xi) = kt \quad (6)$$

The values of rate constants were obtained by carrying out linear regression and were found to be increasing with an increase in temperature. At higher values of conversion ($Xi = 0.60 - 0.95$), R2 (Equation (4)) was the only model agreeing with the experimental data ($R^2 \sim 0.995$) as shown in **Figure 7**. Here again, the values of rate constants varied with temperature, however, indicating an “anti-Arrhenius” behavior with rate constants decreasing with temperature increase, which will be explained later.

Figure 7. Comparison of experimental conversion data ($Xi = 0.6 - 0.95$) with 2D shrinking core model (R2) predictions for CO_2 induced re-oxidation of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSM) oxygen carrier at selected temperatures.

Similarly, among the various models investigated, first order model (F1), 3D Jander’s diffusion (D3) and 3D Ginstling diffusion (D4) models were found to be suitable for

describing the re-oxidation behavior of LCM with $R^2 > 0.99$ at all the temperatures. The obtained correlations between the experimental conversions and model predictions are plotted as a function of time and are provided in **Figure 8**. Even though power law model (PLM) was also explored, it was found to exhibit the lowest agreement with the experimental results obtained for both materials used in this study, for CO_2 induced re-oxidation. The solid-state models exhibiting the lowest correlations for the experimental data of LCM are shown in **Supporting Information Figure S3**.

Figure 8. Comparison of experimental conversion data with model predictions for CO_2 induced re-oxidation of $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LCM) oxygen carrier at selected temperatures. (a) 3D Ginstling diffusion (D4), (b) 3D Jander's diffusion (D3), and (c) first order model (F1). In solid-state reactions, diffusion may play a significant role owing to the mobility of reactant or product constituents through lattice functionalities (vacancies, dislocations or defects). 3D Jander's diffusion (D3) is expressed by taking spherical particle geometry into consideration.

It is a modified version of 3D SCM considering diffusion through a layer of products formed on uniform spherical reactant particles, as rate limiting.^[30,31] While D3 defines the formation of a constant thick product layer, 3D Ginstling diffusion (D4) assumes that the thickness of this product zone increases as reaction proceeds. This latter model also considers the formation of intermediate phases as concentric layers, where appropriate.^[32]

The gXi function for D3 and D4 can be expressed as Equation (7) and (8), respectively.

$$gXi = [1 - (1 - Xi)^{1/3}]^2 = kt \quad (7)$$

$$gXi = [1 - (2Xi/3)] - (1 - Xi)^{2/3} = kt \quad (8)$$

Figure 9. Arrhenius plots for thermochemical CO₂ induced re-oxidation over La_{0.5}Sr_{0.5}MnO₃ (LSM) oxygen carrier. (a) $Xi = 0.05 - 0.6$, (b) $Xi = 0.6 - 0.95$ and (c) LaCo_{0.5}Mn_{0.5}O₃ (LCM) oxygen carrier $Xi = 0.1 - 0.9$.

The models exhibiting superior correlations were used for extracting the kinetic parameters such as apparent activation energies (E_a) and pre-exponential factors (A) from the Arrhenius plots shown in **Figure 9**. For LSM, the values of rate constants were obtained from linear regression of the two regions of solid-state conversions.

Table 2. Kinetic parameters obtained from various mechanistic functions for CO₂ induced re-oxidation of La_{0.5}Sr_{0.5}MnO₃ (LSM) and LaCo_{0.5}Mn_{0.5}O₃ (LCM) oxygen carriers.

Oxygen carrier	Reaction model	T [°C]	k^a [s ⁻¹]	E_a^b [kJ.mol ⁻¹]	A^c [s ⁻¹]
La _{0.5} Sr _{0.5} MnO ₃ (LSM) Xi = 0.05 – 0.6	F1	900	5.61x10 ⁻⁴	4.95	9x10 ⁻⁴
		1050	5.84x10 ⁻⁴		
		1200	6.23x10 ⁻⁴		
	R2	900	2.21x10 ⁻⁴	4.85	3x10 ⁻⁴
		1050	2.29x10 ⁻⁴		
		1200	2.45x10 ⁻⁴		
	R3	900	1.60x10 ⁻⁴	4.76	3x10 ⁻⁴
		1050	1.66x10 ⁻⁴		
		1200	1.77x10 ⁻⁴		
	AE3	900	5.01x10 ⁻⁴	4.47	2x10 ⁻⁴
		1050	5.17x10 ⁻⁴		
		1200	5.51x10 ⁻⁴		
LaCo _{0.5} Mn _{0.5} O ₃ (LCM) Xi = 0.1 – 0.9	R2	900	2.40x10 ⁻⁴	-4.87	2x10 ⁻⁴
		1050	2.24x10 ⁻⁴		
		1200	2.17x10 ⁻⁴		
	F1	900	1.34x10 ⁻⁴	-6.83	7x10 ⁻⁴
		1000	1.27x10 ⁻⁴		
		1100	1.21x10 ⁻⁴		
	D3	900	1.86x10 ⁻⁴	-6.84	9x10 ⁻⁵
		1000	1.75x10 ⁻⁴		
		1100	1.68x10 ⁻⁴		
	D4	900	1.21x10 ⁻⁴	-6.38	6x10 ⁻⁵
		1000	1.15x10 ⁻⁴		
		1100	1.10x10 ⁻⁴		

^{a)}Rate constant; ^{b)}Activation energy; ^{c)}Pre-exponential factor

In the region corresponding to lower values of conversion ($X_i = 0.05$ to 0.6), E_a was found to be low ($\sim 5 \text{ kJ.mol}^{-1}$) compared to the ones reported and was independent of the kinetic model used.^[12] On the other hand, the values of pre-exponential factors (A) were influenced by the model. For higher values of conversion ($X_i = 0.6$ to 0.95), an “anti-Arrhenius” behavior was observed as mentioned above and hence E_a was found to be negative. Even though the entire re-oxidation reaction for LCM was explained appropriately using a single solid-state kinetic model (D3, D4 or F1), the “anti-Arrhenius” behavior with a negative E_a was obtained for this material (Figure 9c). Studies were also performed for this material by separating different regions of solid-state conversions. However, the trends in reaction mechanisms and rate constants remain unchanged. The individual values of rate constants, activation energies and pre-exponential factors are given in **Table 2**.

In general, reaction rate constants increase with respect to an increase in temperature and “anti-Arrhenius” behaviour displaying an inverse relation is not common. However, such a scenario does exist and has been previously reported for a variety of gas phase and solid-state decomposition reactions including thermochemical redox processes.^[12,33-35] Reasons for the existence of such a phenomenon can be multi-fold. Tolman interpretation of activation energy on the basis of statistical mechanics is considered as one straight forward strategy to understand the origin of negative values of E_a .^[36-39] Tolman expression for activation energy is given in Equation (9), where E_T is the average translational energy in all collisions and $E_{T,R}$ is the average translational energy in all collisions that lead to the reaction (it can also be considered as the average energy of the intermediate getting converted into products).

$$E_a = E_{T,R} - E_T \quad (9)$$

This consideration allows the possibility for negative values of E_a provided, $E_{T,R} < E_T$.

Further, enthalpic and entropic aspects were also considered to explain the origin of negative values of E_a . For this, the values of activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$)

were obtained from the Eyring plots shown in **Figure 10**, according to Equation (10) where, K_B is the Boltzmann constant and h is the Planck constant. The values are compiled in **Table 3**.

$$\ln(k/T) = (-\Delta H^\ddagger/RT) + [\ln(K_B/h) + (\Delta S^\ddagger/R)] \quad (10)$$

The inverse correlation of rate constant with respect to temperature resulting in a negative Ea is incompatible with an elementary process occurring in a single step. It can be assumed that the reaction therefore proceeds by following a complex mechanism involving the formation of an intermediate.

Figure 10. Eyring plots for thermochemical CO_2 induced re-oxidation for (a) $Xi = 0.05 - 0.6$, (b) $Xi = 0.6 - 0.95$, over $La_{0.5}Sr_{0.5}MnO_3$ (LSM) oxygen carrier and (c) $Xi = 0.1 - 0.9$ over $LaCo_{0.5}Mn_{0.5}O_3$ (LCM) oxygen carrier.

Revel *et al.* previously reported that such reactions can exhibit negative values for E_a , provided it is accompanied by a negative enthalpy change.^[40] As expected, the values of $\Delta H^\ddagger$ were found to be negative in the present study indicating the reactions are exothermic and are more favoured at low temperatures. The values were found to be influenced by the extent of conversion and composition of the oxygen carrier. Revel *et al.* also stated that the existence of higher number of microstates in the vicinity of intermediate (C), leading back to the reactants instead of leading to products, can also result in a negative activation energy.^[40] Statistically, entropy is proportional to the number of microstates. The negative values of $\Delta S^\ddagger$ obtained in the present study indicate an associative mechanism occurs and the products are in a more ordered state. These values remained constant independent of the extent of conversion and the composition of the oxygen carrier.

Table 3. Kinetic parameters obtained from various mechanistic functions for CO₂ induced re-oxidation of La_{0.5}Sr_{0.5}MnO₃ (LSM) and LaCo_{0.5}Mn_{0.5}O₃ (LCM) oxygen carriers

Oxygen carrier	Reaction model	$\Delta H^\ddagger$ [kJ.mol ⁻¹] ^{a)}	$\Delta S^\ddagger$ [kJ.K ⁻¹ mol ⁻¹] ^{b)}
La _{0.5} Sr _{0.5} MnO ₃ (LSM) Xi = 0.05 – 0.6	F1	-5.93	-0.32
	R2	-6.02	-0.33
	R3	-6.12	-0.33
	AE3	-6.40	-0.32
La _{0.5} Sr _{0.5} MnO ₃ (LSM) Xi = 0.6 – 0.95	R2	-15.75	-0.34
LaCo _{0.5} Mn _{0.5} O ₃ (LCM) Xi = 0.05 – 0.95	F1	-17.36	-0.33
	D3	-17.36	-0.34
	D4	-16.91	-0.34

^{a)}Enthalpy of activation; ^{b)}Entropy of activation

For LSM, depending on the extent of conversion, F1 and R2 solid-state models most appropriately described the CO₂ induced re-oxidation reaction mechanism. However, at lower conversion region (Xi = 0.05 – 0.6), R2, R3 and AE3 models also exhibited good agreement

with the experimental data, with constant values of activation energies (Ea) and activation enthalpies ($\Delta H^\ddagger$). Even though Ea remained constant at higher values of conversions, a significant increase in $\Delta H^\ddagger$ was observed. The values of pre-exponential factors (A) were found to depend both on the model used and on the extent of conversion. On the other hand, D4 model most suitably described the entire re-oxidation reaction ($X_i = 0.1 - 0.9$) in the case of LCM, along with F2 and D3 models. In this case, the values of Ea , A and $\Delta H^\ddagger$ displayed similar trends as observed in the case of LSM. For both oxygen carriers explored in this study, the activation entropies ($\Delta S^\ddagger$) remained constant regardless of the composition or extent of conversion.

In thermochemical reactions, deactivation effects can result in negative activation energy. For instance, maximum rate can be achieved at a particular temperature so that further increase in temperature has a minor effect on the value of rate constant. In conjugation, long term exposure to high temperatures can result in sintering and agglomeration of solid particles and thereby limiting the concentration of accessible active sites for the gaseous reactant. Thus, lowering of rate constants to a small extent can be the overall consequence. The transport of the reactant and product species is taking place through grain boundaries, structural dislocations, or vacancy sites. These low resistance diffusion paths can be deactivated or blocked to some extent, considering the possibility of sintering in the case of grain boundaries and formation of parent oxide by consuming oxygen in the case of dislocations and vacancies. This limited access of the gaseous components to and from the active sites can also result in the lowering of rate constants. Intrinsic mechanistic features apart from deactivation effects can also lead to an “anti-Arrhenius” behavior and negative activation energy. Such effects are previously reported for low temperature reactions such as in CO oxidation and in organocatalysis.^[41,42] Similarly, unexpected mechanistic abnormalities or side reactions may possibly arise in thermochemical metal oxide redox reactions. For instance, during the re-oxidation reaction of LSM/LCM, after consuming a certain amount of oxygen in the lattice

vacancies, a portion of surface oxygen or adsorbed oxygen may be released back and is getting recombined with CO forming CO₂. Such an undesired side reaction can be catalytically promoted by the transition metal (Mn and Co in the present study) in the perovskite B-site. For instance, water gas shift (WGS) is one example where such CO₂/CO equilibrium exists at high temperature.^[43,44] In the present study, the presence of such an equilibrium may influence the mass variation and hence the rate constant can be lowered. However, further detailed investigations incorporating advanced methodologies (operando, DFT, etc) are necessary to experimentally confirm such aforementioned possibilities.

3. Conclusion

Perovskite oxides are widely considered as alternatives to replace CeO₂ oxygen carrier for solar thermochemical fuel production. In the present study, the solid-state re-oxidation kinetics of La_{0.5}Sr_{0.5}MnO₃ and LaCo_{0.5}Mn_{0.5}O₃ were examined. These two compositions are considered as promising A and B-site substituted perovskites candidates for thermochemical redox reactions. Several classical kinetic models were utilized to derive the mechanism for CO₂ induced re-oxidation reactions over these materials. Results indicate that the most suitable model describing the re-oxidation mechanism varied depending on the composition of the oxygen carrier. A two-step reaction mechanism was observed for La_{0.5}Sr_{0.5}MnO₃ where first order model (F1), 2D and 3D variants of shrinking core model (R2 and R3) and 3D nucleation and nuclei growth model (AE3) were found to represent low conversion region ($X_i = 0.05 - 0.6$) in LSM, where F1 model exhibited the best fit. For higher values of conversion ($X_i = 0.6 - 0.95$), R2 model was the most appropriate. On the other hand, for B-site substituted perovskite (LaCo_{0.5}Mn_{0.5}O₃), diffusion controlled (D4) mechanism was favored. The values of apparent activation energies were found to be remarkably low ($\sim 5 \text{ kJ.mol}^{-1}$) for low values of conversion of LSM and even negative for higher conversion region of LSM, as well as for the entire re-oxidation reaction ($X_i = 0.1 - 0.9$) of LCM. The values of enthalpies of activation ($\Delta H^\ddagger = -6 \text{ to } -18 \text{ kJ.mol}^{-1}$) were found to depend on the extent of conversion and

composition, whereas entropies of activation ($\Delta S^\ddagger = -0.33 \text{ kJ.K}^{-1}.\text{mol}^{-1}$) remained constant.

The reason for such complex behavior can be multifold and can probably be attributed to the diffusion limitations due to thermal stability aspects, variations in lattice functionalities, the occurrence of undesired side reactions or a combination of these effects.

4. Experimental Section

Synthesis of Materials: Conventional solid-state method was applied to synthesize well crystallized and phase pure perovskite structured mixed metal oxides. Binary oxides and carbonates in appropriate stoichiometries were used as precursors. SrCO_3 , Co_3O_4 , and MnO_2 were used as received. La_2O_3 was pre-treated at 950°C for 6 h in order to decompose the possible La(OH)_3 contamination. Appropriate quantities of precursors based on the final perovskite composition were ground well and calcined initially at 1000°C . Simultaneously, a final calcination step, depending on the desired phase formation and structure stabilization, was carried out for several hours.

Characterization: X-ray diffraction (XRD) patterns were recorded with a Philips PW 1820 diffractometer with the $\text{Cu K}\alpha$ radiation (0.15418 nm , angular range = $20\text{-}80^\circ 2\theta$, steps = $0.02^\circ 2\theta$, recording time = 2 s). Phase identification was carried out by comparison with standard diffraction patterns (powder diffraction file PDF-2, International Centre for Diffraction Data, ICDD). Information regarding particle morphology and surface microstructure were determined from SEM images obtained using a high-resolution field emission scanning electron microscope (FE-SEM, Hitachi S4800).

Redox Experiments: Thermochemical re-oxidation rates in presence of CO_2 of the synthesized perovskite oxygen carriers were determined by performing thermogravimetric (TG) analyses. The amounts of CO evolved were obtained from sample mass variations. All the reduction and re-oxidation experiments were performed using a SETARAM SETSYS Evolution device ($0.03 \mu\text{g}$ resolution) equipped with a platinum crucible to continuously monitor the sample mass as a function of temperature and atmosphere. The balance (fitted with a beam articulated

on a torsion ribbon) displays high stability and sensitivity (with a typical mass drift of only $0.1 \mu\text{g}\cdot\text{h}^{-1}$) thanks to a high-performance, optical and electronic detection fitting. The intrinsic uncertainty could be considered minor when compared with the reduction capabilities of the samples. Indeed, for cycles lasting around 7 hours, the uncertainty on the mass change is weak (below $1 \mu\text{g}$) compared to the mass variation of the samples. Blank run correction (using empty crucible) was done to eliminate the small baseline drift during non-isothermal heating caused by thermal gas expansion and buoyancy effects on the crucible. Sample masses of approximately 100 mg were used for each analysis. Thermal reduction step was performed under an Ar flow of $0.020 \text{ Nl}\cdot\text{min}^{-1}$ (99.999% purity, $<2 \text{ ppm O}_2$) at a fixed temperature of 1400°C during 45 min of temperature plateau. Re-oxidation of the partially reduced oxides was carried out under CO_2 (50% in Ar) at selected temperatures (900 – 1200°C) during 40–60 min. This re-oxidation temperature was selected based on the material composition, optimum performance, and stability. All heating and cooling steps were performed with a ramp rate of $20^\circ\text{C min}^{-1}$. The O_2 release during reduction induced a mass loss (Δm_{red}), whereas O atom incorporation during re-oxidation induced a mass increase (Δm_{ox}). These mass variations were used to determine the mole amounts of O_2 released during thermal reduction and CO produced during re-oxidation.

$$n_{\text{O}_2} = \Delta m_{\text{red}} / M_{\text{O}_2} \quad (12)$$

$$n_{\text{CO}} = \Delta m_{\text{ox}} / M_{\text{O}} \quad (13)$$

For each cycle, the amount of oxygen lost during the reduction was associated with the amount of CO produced in the subsequent step. This is the basis for the materials performance evaluation in each cycle, which is of course dependent on the reaction duration, but the goal was here to assess the re-oxidation potential for a given material.

Kinetic Data Processing: Thermochemical reduction temperature was fixed at 1400°C and CO_2 induced re-oxidation reactions were carried out at selected temperatures (900 – 1200°C).

The solid conversion fractions were calculated using the following equation where X_i denotes the extent of conversion during re-oxidation in presence of CO_2 .

$$X_i = (\Delta m_t / \Delta m) \quad (14)$$

where, Δm_t is the mass gain during re-oxidation at a specific time. The intrinsic kinetics of the gas–solid reaction can be formulated considering an overall reaction rate being a function of the degree of re-oxidation of solid material (fX_i) and the composition of the gas-phase (fG), as represented by the following equation.

$$dX_i/dt = k \cdot fX_i \cdot fG \quad (15)$$

where, X_i is the extent of reaction which can be expressed in terms of the mass variations of the solid material during reduction or re-oxidation as expressed in Equation (14). The function fG in Equation (15) can be lumped in a single pseudo-constant given that all the reactions were carried out at same feed flow rate and oxygen partial pressure. Thus, Equation (15) can be simplified into:

$$dX_i/dt = k \cdot fX_i \quad (16)$$

The integral form of Equation (16) can be expressed as:

$$gX_i = \int_0^x \left(\frac{dX_i}{fX_i} \right) \quad (17)$$

In the present study, several solid-state kinetic models including reaction order, shrinking core, nucleation and diffusion were chosen to determine the best fit for experimental data and thereby describing the kinetic rate law and reaction mechanism. In all these cases, the rate constant, k , can be expressed as a function of temperature in the form of Arrhenius equation shown below.

$$k = A \cdot \exp(-Ea/RT) \quad (18)$$

One method for fitting the model to the experimental data is by determining the linearity of gX_i versus time. The slope of this function results in the reaction rate constant (k). For evaluating the other kinetic parameters, such as apparent activation energy (Ea) and pre-

exponential factor (A), the reaction rate constant must be obtained for different temperatures.

Then, from the Arrhenius plot (Equation 18), the values of E_a and A for the re-oxidation of oxygen carriers can be obtained from the slope and intercept, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. This section includes additional information regarding the comparison between experimental conversion data with reaction models

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