Reduction kinetics of lanthanum ferrite perovskite for the production of synthesis gas by chemical-looping methane reforming

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HIGHLIGHTS

- Kinetic of reduction of LaFeO₃ oxygen carrier for CLMR was determined.
- The 2-D nuclei growth model best describes solids conversion evolution with time.
- Model validity is verified by continuous flow reaction and sequential redox cycles.
- Activation energies for the rate constants were estimated.

GRAPHICAL ABSTRACT

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ABSTRACT

The reduction kinetics of LaFeO₃ oxygen carrier for the production of synthesis gas by chemical-looping methane reforming (CLMR) is investigated in the present work. The stoichiometric relationship between oxygen carrier and methane in chemical-looping process is established by temperature programmed surface reaction (TPSR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) characterization. The effects of reduction conditions, namely, gas to solid molar ratio, temperature and sequential redox reaction on the oxygen carrier conversion are investigated. The results from Hancock and Sharp method suggest that the phase boundary control is likely to be dominant. The power law model (PLM), shrinking core model (SCM), as well as nucleation and nuclei growth model (NNGM) are considered to interpret the reduction kinetics of LaFeO₃ with methane to synthesis gas. The obtained results show that the 2-D NNGM best describes the experimental data providing parameters with adequate statistical fitting indicators. The model validity is also verified by the data from continuous flow reaction and sequential redox cycles to simulate chemical-looping methane reforming process. The apparent activation energy is estimated and compared with values from the literature data.

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1. Introduction

Efficient and environmental friendly conversion of methane into synthesis gas (syngas, CO+H₂) is a topic of practical relevance for the production of hydrogen, chemicals, and synthetic fuels

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(Tanaka et al., 2009). At present, the efficiencies of the steam methane reforming processes are limited owing to the intensely endothermic reaction and high steam to methane ratio required. One of the potentially attractive ways of syngas production is partial oxidation of methane (POM) process without external heat supply. However, a major barrier for this process is the rapid catalyst deactivation caused by coke formation, mostly for nickel-based catalysts (Kim et al., 2009; Enger et al., 2008). Another

Nomenclature

A	pre-exponential factor (model specific)	p_{CH_4}	partial pressure of methane (kPa)
$C_{CH_4 0}$	initial concentration of methane (mol/m ³)	$-r_{CH_4 robs}$	observed reduction rate (mol/m ² s)
$C_{CH_4 b}$	concentration of methane in the bulk fluid (mol/m ³)	$-r'_{CH_4 robs}$	observed rate of the reduction reaction (mol/g/s)
$C_{CH_4 s}$	concentration of methane at the surface of the oxygen carrier (mol/m ³)	R	gas constant (J/mol/K)
C_{WP}	Weisz–Prater parameter	S_{ex}	external surface area per gram of sample (m ² /g)
D	diameter of oxygen carrier (μm)	T	temperature (K)
D_{AB}	diffusivity for methane in argon (m ² /s)	$W_{CH_4 r}$	radial flux of methane (mol/m ² s)
D_{eff}	effective diffusivity (m ² /s)	w_p	mass of oxide carrier loaded into the reactor (g)
E_a	activation energy (kJ/mol)	X_{CH_4}	conversion of methane (%)
$f(\alpha)$	reaction model	A	conversion of oxygen carrier (%)
$f(p_{CH_4})$	function of methane partial pressure in the gas phase	β	constant which is partially dependent upon the nucleation frequency and rate of grain growth
$g(\alpha)$	integral form of the reaction model	P	density of oxygen carrier (kg/m ³)
M_p	molecular weight of oxygen carrier (kg/mol)	k	rate constant (model specific)
$N_{CH_4, 0}$	initial number of moles injected into the reactor (mol)	n	Avrami constant
		T	reduction time (s)

challenge by POM process is the costly air separation unit for pure oxygen and high possibility of gas explosion by directly contact of oxygen and methane at high temperature (Choudhary and Choudhary, 2008; Rostrup-Nielsen et al., 2008). Applying the chemical looping methane reforming (CLMR) concept to POM enables an opportunity to resolve the two issues by spatially separating CH₄ conversion into two half-steps over the fuel reactor and air reactor. The CLMR process eliminates the expensive air separation and mixing unit, and fulfills the heat balance between the endothermic reduction reaction in fuel reactor and exothermic oxidation reaction in air reactor by the circulating oxygen carrier (de Diego et al., 2008; Dueso et al., 2012). The reduction of oxygen carrier by methane shows the potential for a new green technology of syngas production without using any catalyst and its deactivation problem.

The key issue for large-scale application of CLMR process is the oxygen carrier with suitable properties. Several critical screening criteria have been addressed which include reversible oxygen storage capacity, reactivity toward both fuel and oxidant, attrition resistance, agglomeration and carbon deposition, as well as the environmental and economic impacts (Tang et al., 2015). It is generally accepted that NiO possesses sufficient activity among the transient metal oxides, but the carbon formation with Ni-based oxygen carriers is prominent in chemical-looping methane combustion (CLMC), and thus is observed mostly at the end of reduction reactions (Rydén et al., 2008a; Cabello et al., 2014a). The challenge of NiO based redox catalysts, however, is their high tendency for coke formation, high cost, and health concerns (Adanez et al., 2012; Neal et al., 2014). Fe-based oxides have the advantages of being cheaper, low agglomeration, high melting point and more environmentally benign (Cabello et al., 2014a; Adanez et al., 2012; Neal et al., 2014, 2015; Shafieifarhood et al., 2014; Galinsky et al., 2015). However, iron oxide based redox catalysts are not particularly active for methane oxidation (Cabello et al., 2014a; Shafieifarhood et al., 2014), and tend to have low selectivity toward methane partial oxidation. Notably, the reactivity and selectivity in CLMR process can be improved by combining different materials to bring synergetic effect or form solid solution (spinel, perovskite, et al.) (Cabello et al., 2014a; Neal et al., 2014, 2015; Bhavsar and Vesar, 2013; Zhu et al., 2014; Chen et al., 2014). As mentioned above, although many work to increase the reactivity and syngas selectivity have been carried out for a long time, the reduction kinetics of oxygen carriers using methane as fuel at representative conditions of CLMR system has been seldom investigated (Dueso et al., 2012; Rashidi et al., 2013a,

2013b). Many models have been used to describe the conversion-time profiles of noncatalytic gas–solid reactions in the literature. The most frequently used models are the shrinking core model (SCM) and nucleation and nuclei growth model (NNGM), which have also been done in the past about the reduction kinetic determination of supported or un-supported metal oxides for CLMC (Hossain and de Lasa, 2008; Sedor et al., 2008; Monazam et al., 2013; Nasr et al., 2014; Lario et al., 2013; Hossain et al., 2010a; Hossain and de Lasa, 2010b; Hossain and de Lasa, 2007). However, the application of the experience achieved for CLMC can not be directly applied to the reactions involved in the CLMR process for several reasons: (i) the composition and type of oxygen carriers are distinct from CLMC; (ii) the oxidized and reduced state can not be the same as that for CLMC; (iii) the experimental condition (e.g. temperature, gas composition, gas to solid ratio, desired product) are usually different with those required for CLMR. Rashidi et al. (2013b) found only a small induction period in the reduction of unsupported nickel oxide with methane, and neglected it in the modified grain model for spherical grain geometry. However, an induction period was indeed observed during the reduction of iron ore, Ni-based oxygen carrier and LaMnO₃ perovskite (Nasr and Plucknett, 2014; Sarshar et al., 2013; Zafar et al., 2007). Sarshar and Kaliaguine (2013) found that both SCM and NNGM yield poor fits of the reduction kinetic data, and the introduction of an induction time in kinetic model will improve the valid estimation. These results implied that it is very necessary to determine different reduction kinetic parameters for each oxygen carrier, which depends on the oxygen-transport capacity and reactivity of the oxygen carrier.

As excellent reduction–oxidation properties, high reversible oxygen mobility, and chemical and thermal stability, perovskite-based oxygen carriers become more attractive in CLMR process (Mihai et al., 2012; Dai et al., 2006a, 2006b; García et al., 2010; Mihai et al., 2011; Nalbandian et al., 2011; Rydén et al., 2008b). The desirable properties of perovskite (e.g. metal ions, binding energy and oxygen diffusion in the lattice) can be tailored by selectively changing A and B cations (Mihai et al., 2012). Recently, perovskite-type LaFeO₃-based oxygen carriers and its substitution in A and/or B sites exhibit high catalytic activity with high selectivity towards CO/H₂ in CLMR process (Mihai et al., 2012; Dai et al., 2006a, 2006b; García et al., 2010; Mihai et al., 2011; Nalbandian et al., 2011; Rydén et al., 2008b; Zeng et al., 2003), which fuels the desire to investigate the reduction kinetics of LaFeO₃ oxygen carriers with methane in order to estimate the relevant design parameters for CLMR process, e.g., solids circulation flow rate or solids

inventory in the fuel reactor. Herein, the reduction kinetics of LaFeO₃ oxygen carrier under different reduction temperature and gas to solid molar ratios were investigated. Three kinetic models were compared on the bases of their ability to accurately describe the experimental data: the power-law relation, the shrinking core model, and the nucleation and nuclei growth model. The kinetic data obtained in this work will be implemented in a reactor model for the prediction, design and optimization purposes of a CLMR system with LaFeO₃ perovskite as the oxygen carrier.

2. Experimental

2.1. Preparation of oxygen carrier

The LaFeO₃-perovskite oxide was prepared by the sol-gel method. Typically, the La and Fe nitrates (La/Fe=1.0, atom ratio) were completely dissolved in deionized water. Then, glycine solution was added dropwise to the mixed solution with stirring at a ratio NH₃/NO₃[−]=1.05. The mixed solution was agitated at 353–363 K to form a viscous gel, and dried at 353 K for 24 h. The resulted gel was placed in a stainless steel sealed vessel at 523 K for 30 min to obtain a brown powder precursor. The precursor was calcined at 1173 K for 10 h, and then were tableted, crushed, and sieved.

2.2. Characterization of oxygen carrier

Powder X-ray diffraction (XRD) was performed on a ShiDU XRD-6000 diffraction with Ni-filtered Cu Kα radiation. The BET surface area was 6.08 m²/g by N₂ adsorption/desorption at 77 K using a gas sorption analyzer NOVA 1200. Investigations of the morphology were carried out on a HITACHI S-4800 scanning electron microscope (SEM) and JEOL-2100 transmission electron microscopy (TEM). The particle size distribution of the nano-powder was measured by a laser particle size analyzer (Mastersizer 2000 Particle Analyzer, Malvern Instruments Ltd.). The X-ray photoelectron spectrum (XPS) was carried out on a VGESCA LAB 210 system using Mg K radiation. All binding energies were calibrated to the C1s peak at 284.6 eV.

A micromeritics chemisorb 2720 system (Micromeritics Instrument Corp.) was used to investigate oxygen desorption (O₂-TPD) and hydrogen reduction (H₂-TPR) tests. Prior to O₂-TPD, 125 mg sample was pretreated in 5 vol% O₂/He at 423 K for 3 h. Then, After cooling to room temperature, the sample was heated from room temperature to 1233 K at a rate of 10 K/min in pure He. The desorbed oxygen was continuously monitored and quantified by a thermoconductivity detector (TCD). The H₂-TPR was carried out on the same apparatus as in O₂-TPD. 196 mg sample was placed in a quartz reactor, pretreated under a flow of 20 mL/min (20 vol% O₂ in He) at 423 K for 2 h, and cooled down to room temperature. The H₂-TPR was then carried out under a 10 mL/min flow of 5 vol% H₂ in Ar. The temperature was increased from room temperature to 1233 K at a rate with a ramp of 10 K/min. The consumption of hydrogen was monitored and quantified using a TCD on the basis of the calibrations at various weight of pure CuO. Temperature programmed surface reaction with methane (CH₄-TPSR) was performed on a quartz fixed-bed microreactor (6 mm i. d.) packed with 250 mg samples. The sample was dehydrated for 1 h at 423 K in pure Ar, then the temperature was increased at a rate of 15 K/min under 11 vol% CH₄ in Ar with a flow of 26 mL/min. The composition of the effluent gas from the reactor was monitored by an on-line quadrupole mass spectrometer.

2.3. Reactivity tests of oxygen carrier

In continuous flow reaction, the oxygen carrier was placed in a fixed-bed microreactor with inner diameter of 6 mm and a height of 580 mm, and was heated to reaction temperature for pretreatment with 11 vol% O₂/Ar (23 mL/min) for 30 min. Then the reactant gas (11 vol% methane in argon, 23 mL/min) was introduced. Sequential redox cycles were performed at 1173 K between reductive atmospheres (11 vol% CH₄ in He, 23 mL/min) and oxidative atmospheres (11 vol% O₂ in Ar, 23 mL/min) to simulate fuel reactor and air reactor. The offgas composition from the reactor was monitored by an on-line quadrupole mass spectrometer. The mass spectrometer signals were calibrated before each experiment by using a calibration gas with known composition. All gas-phase components were calibrated except water, which was calculated based on the mass balance. Blank experiments using an inert quartz at identical conditions indicated low contribution of gas-phase reactions (< 2% methane conversion of gas-phase reaction) in the present work. The accumulated amount of oxygen removal in the reduction step, total oxygen consumption, oxygen consumption to carbon oxidation were estimated based on mass balance on carbon and oxygen using Ar as the internal stand, which were closed to within ± 5% in all experiments.

The methane conversion (Eq. (1)) and the CO selectivity (Eq. (2)) as well as the hydrogen (Eq. (3)), carbon balances (Eq. (4)) and oxygen vacancy concentration (Eq. (5)) were calculated according to the following equations:

$$X_{CH_4} = \frac{N_{CH_4^{in}} - N_{CH_4^{out}}}{N_{CH_4^{in}}} \times 100\% \quad (1)$$

$$S_{CO} = \frac{N_{CO^{out}}}{N_{CO^{out}} + N_{CO_2^{out}}} \times 100\% \quad (2)$$

$$4N_{CH_4^{in}} = 4N_{CH_4^{out}} + 2N_{H_2^{out}} + 2N_{H_2O^{out}} \quad (3)$$

$$N_{CH_4^{in}} = N_{CH_4^{out}} + N_{CO^{out}} + N_{CO_2^{out}} + N_{C^{out}} \quad (4)$$

$$\text{Oxygen vacancy concentration} = \frac{N_{CO^{out}} + 2N_{CO_2^{out}} + N_{H_2O^{out}}}{n} \quad (5)$$

where X_{CH_4} is the methane conversion, S_{CO} is CO selectivity, N_i is mole of compound i within t (mmol), and n is the mole of oxygen carrier.

3. Results and discussion

3.1. Materials characterization

The XRD spectrum in Fig. 1 shows single-phase perovskite with orthorhombic structure for fresh LaFeO₃ (JCPDS Card nos. 37-1493). The uniform nanostructured textural background with pseudo-spherical particles of average sizes of 170 nm was observed in SEM and TEM images, where aggregation of individual nanoparticles is occurred (Fig. S1A–B). The size distribution profile in Fig. S1C, represents typical particles between 10 and 1000 μm. The result of O₂-TPD indicates that the LaFeO₃ perovskite does not have an obvious tendency to release gaseous oxygen with oxygen uncoupling (Fig. S1D). A small amount of Fe⁴⁺ in the perovskite can be reduced to Fe³⁺ (~0.054 mmol/g) at low temperature

Fig. 1. X-ray diffraction patterns of (a) fresh LaFeO_3 , (b) after H_2 -TPR to 1173 K, (c) after TPSR from room temperature to 1073 K, (d) to 1145 K and (e) to 1173 K (JCPDS 37-1493 for perovskite LaFeO_3 ; JCPDS 36-1481, blue bar for $\text{La}(\text{OH})_3$; JCPDS 06-0696, purple bar for metallic Fe).

(~680 K) in H_2 -TPR (Fig. S1D) (Ciambelli et al., 2001; Chen et al., 2013), which can be further reduced into Fe^{2+} (0.185 mmol/g), declaring a limited reducibility of Fe^{3+} ions in perovskite structure, further confirmed by XRD characterization due to the absence of new phase (Fig. 1). For the peak within low temperature (~680 K), although there are controversies about the reduction of Fe^{4+} or the iron species on the surface and the removal of surface oxygen (Ciambelli et al., 2001; Chen et al., 2013; Velichkova et al., 2013), the nonstoichiometric composition contains oxygen vacancies that can be filled up is the only reason for the presence of Fe^{4+} in order to electrically balance, verified the essentially uniformity about the attribution of the peak within low temperature. The chemical formula is deduced as $\text{LaFe}_{0.013}^{4+}\text{Fe}_{0.987}^{3+}\text{O}_{3.0065}$ according to the H_2 -TPR.

In order to decide the relationship between the structure and available oxygen, the combination of CH_4 -TPSR, XRD and XPS characterization was used to explore the losses of oxygen species, catalyst structure and surface state. In CH_4 -TPSR, the main products are CO and H_2 , while only small amounts of CO_2 and H_2O are detected in Fig. 2. As the temperature higher than 1000 K, more CH_4 is converted to CO and H_2 . The CO intensity reaches its peak at 1145 K, then gradually decline; however, the H_2 intensity does not drop with CO intensity, suggesting that carbon deposition occurs on the LaFeO_3 surface (Dai et al., 2006b). According to XRD, the perovskite structure is still maintained until to 1140 K (Fig. 1). However, when the temperature is further increased to 1173 K, new characteristic peaks for $\text{La}(\text{OH})_3$, trace La_2O_3 and metallic Fe will present, indicating structure collapse of perovskite. Although the metallic Fe can be oxidized to Fe_2O_3 during cyclic oxidation–reduction process, the selectivity of CO will be poor (Monazam et al., 2013; Piekiet al., 2012; Cabello et al., 2014b; Bhavsar et al., 2014). Assuming that one monolayer of oxygen amounts to $4 \mu\text{mol}/\text{m}^2$ (Kaliaguine et al., 2001), the calculated number of O atoms is about $264 \mu\text{mol}/\text{m}^2$ involving in CLMR process before carbon deposit occurs, which is corresponding to 66 monolayers. We also use XPS to explore the surface state during CH_4 -TPSR (Fig. 3). The position and shape of $\text{La}3d$ peaks agree well with the presence of La (III) compounds: the well evident shake-up contributions at ~833.7 eV and ~850.6 eV. No significant differences are observed in the $\text{La}3d_{5/2}$ doublets (La_2O_3 at 838.4 eV and $\text{La}(\text{OH})_3$ at 833.9 eV). The high-resolution XPS of $\text{Fe}2p$ exhibits two peaks at

Fig. 2. CH_4 -TPSR over LaFeO_3 -perovskite oxygen carrier.

710.1 and 723.7 eV, which correspond to the peaks of $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$ in fresh LaFeO_3 , respectively. After exposing to methane, $\text{Fe}2p_{3/2}$ peak widens and shake-up satellite decreases, which indicates that surface Fe^{3+} species gain electron and gradually reduce to Fe^{2+} with methane (Gao et al., 2013). The O1s XPS peaks at 529.0 is attributed to lattice oxygen in perovskite oxide (metal–oxygen bond), while 531.1 and 532.4 eV are assigned to weakly bound oxygen on the surface (O_2 species that are molecularly adsorbed in the subsurface regions of oxygen-deficient perovskite-type compounds) or/and to the surface hydroxyls (Jirátová et al., 2009).

According to CH_4 -TPSR, XRD and XPS characterization, the maximum amount of oxygen that can release without structure collapse, namely the capacity of reversible oxygen storage, is found to be about 0.39 mol/mol oxygen carriers. The stoichiometric reaction between CH_4 and oxygen carrier can be expressed as follows:

The reaction represents only selective oxidation, and ignores complete oxidation to CO_2 and H_2O , because the amount for complete oxidation is much smaller than that for selective oxidation. Thus, the neglect of the complete oxidation in Eq. (6) will not lead to significant errors.

The solid conversion of perovskite-oxide LaFeO_3 oxide ($\alpha_{(t)}$) is calculated as:

$$\alpha_{(t)} = \frac{N_{\text{CH}_4,0} X_{\text{CH}_4}}{0.39 \frac{w_p}{M_p}} \quad (7)$$

where $N_{\text{CH}_4,0}$ is the mole of methane injected into the reactor for a certain time (t), X_{CH_4} is the conversion of methane, w_p is the mass of LaFeO_3 perovskite loaded into the reactor, and M_p is the molecular weight of LaFeO_3 perovskite.

3.2. Reactivity and stability toward CLMR

3.2.1. Effect of reduction parameters on oxygen carrier conversion

Fig. 4A shows the effect of the gas to solid molar ratio on the oxygen carrier conversion (α), indicating sigmoidal shapes for all curves. High gas to solid molar ratio is necessary to increase the

Fig. 3. High-resolution XPS spectra of LaFeO₃ oxygen carrier, (1) fresh sample, (2) after TPSR from room temperature to 1145 K, and (3) from room temperature to 1173 K.

Fig. 4. Oxygen carrier conversion vs. time for (A) varying gas to solid molar ratios at 1173 K and (B) reaction temperatures with gas to solid ratio of 26.3.

oxygen carrier conversion at short reduction time, which has been observed in our previous work (Dai et al., 2012). The reduction rate of LaFeO₃ oxygen carrier is accelerated with the reaction time, and the trend is more dominant at high gas to solid molar ratio, which is clearly different from the two-stage reduction process over Ni-based oxygen carriers, characterized by the fast NiO reduction and low nickel aluminate reactivity (Dueso et al., 2012). The oxygen carrier conversion (α) for the various temperatures under gas to solid molar ratio of 26.3 is presented in Fig. 4B. The oxygen carrier conversion (α) slowly increases with reaction time at 1073 and 1123 K, whereas it sharply increases at the reaction temperature of 1173 and 1223 K. The sigmoidal shapes may be divided into two distinct regions. In the first region, the conversion of LaFeO₃ oxygen carrier is slowly increased due to the presence of an induction period ($0 < \alpha < 0.10$). The length of induction period is temperature dependent, which becomes longer at lower temperature (Liu et al., 2001). The dissociation of CH₄ and reaction rate is accelerated with the active centers increased in the second region. The acceleration ($\alpha > 0.10$) is more dramatic under high temperature, suggesting more available oxygen species at high temperature for the same reduction time. In this work, we don't observe the deceleration or decay period, because the reduction time is controllable to avoid the carbon deposit and structure collapse of oxygen carrier.

3.2.2. Stability test by sequential reduction–oxidation (redox) cycles

Fig. 5 depicts the responses of reactants and products during the redox reaction between O₂/Ar oxidation for 10 s and CH₄/He reduction for 30 s over the LaFeO₃ oxygen carrier at 1173 K. Only a small amount of methane is oxidized to CO₂ at the first cycle, and then CO and H₂ are dominant products, which further verifies the feasibility in Eq. (6). The H₂/CO ratio is about 1.95 and close to the stoichiometric ratio of the POM. The CO selectivity keeps more than 96%. The oxygen species consumed at reductive atmospheres (CH₄/He) can be replenished at oxidative atmospheres for a short time (10 s). The oxygen carrier conversion (α) remains at a level of ~6% during the whole redox experiment. It seems that LaFeO₃ oxygen carrier display a higher stability under CLMR conditions (Figs. S2 and S3), suggesting that the available oxygen over each successive reduction step is essentially not affected by the number of oxidation–reduction cycles.

Fig. 5. Sequential redox reaction to simulate chemical-looping methane reforming process over LaFeO₃ oxygen carrier at 1173 K.

Table 1

Parameters used to evaluate effects of diffusion limitations at 1173 K.

Parameters used to evaluate effects of external diffusion limitations		Parameters used to evaluate effects of internal diffusion limitations	
D (μm)	1000	D (μm)	1000
w _p (g)	0.25	w _p (g)	0.25
D _{AB} (m ² /s)	2.241 × 10 ⁻⁴	-r' _{CH4r} (mol/g s)	8.31 × 10 ⁻⁶
C _{CH4b} (mol/m ³)	4.496	ρ	1350
C _{CH4s} (mol/m ³)	0	D _{eff} (m ² /s)	2.241 × 10 ⁻⁵
W _{CH4r} (mol/m ² s)	2.015	C _{CH4b} (mol/m ³)	4.496
-r' _{CH4robs} (mol/m ² s)	1.37 × 10 ⁻⁶	C _{WP}	2.784 × 10 ⁻⁵

Table 2

Commonly kinetic models for gas–solid reaction.

Kinetic model	Kinetic mechanism	Differential forms ($f(\alpha) = \frac{1}{k} \frac{d\alpha}{dt}$)	Integrated forms ($g(\alpha) = kt$)
Kinetic-order models	1st order	$1 - \alpha$	$-\ln(1 - \alpha)$
	2nd order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
Shrinking core model	2-D	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
	3-D	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
Nucleation model	2-D	$2(1 - \alpha)[\ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$
	3-D	$3(1 - \alpha)[\ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{2/3}$

Fig. 6. Plots obtained for varying different temperature following the Hancock and Sharp method ($R^2 > 0.98$).

3.3. Kinetic model

3.3.1. Rate-limited step

Heterogeneous process generally involves three stages: external mass transport (reactant diffusion to surface), chemical reaction and internal mass transport (reactant diffusion to bulk). During kinetic determination, external and internal diffusion should be avoided, which could limit the chemical reaction rate. Frossling correlation and Weisz–Prater criterion can be used to assess them, respectively (Sedor et al., 2008; Piekiet et al., 2012).

For external diffusion limitation and negligible shear stress, the radial flux of methane (W_{CH4r} , mol/m² s) can be calculated on the basis of the Sherwood number with Frossling's dimensionless correlation, which then compares with the observed reduction rate ($-r'_{CH4robs}$, mol/m² s). The W_{CH4r} and $-r'_{CH4robs}$ can be expressed as follows.

$$W_{CH4r} = \frac{2D_{AB}}{D}(C_{CH4b} - C_{CH4s}) \quad (8)$$

$$-r'_{CH4robs} = \frac{N_{CH40} dX_p}{w \cdot S_{ex} dt} \quad (9)$$

The diffusivity of methane in argon (D_{AB}) inside the reactor at different temperature and atmospheric pressure was calculated using the Fuller, Schettler and Giddings method (Sedor et al., 2008), and was shown in Table 1 and Table S1. D_{AB} at 1173 K was calculated as 2.241×10^{-4} m²/s. The $-r'_{CH4robs}$ was calculated on the basis of the oxygen carrier conversion, external surface area of the carrier, and the number of moles of methane injected during a certain time (t).

For internal diffusion limitation, the Weisz–Prater can be expressed as follows.

$$C_{WP} = \frac{-r'_{CH4robs} \cdot \rho \cdot (D/2)^2}{D_{eff} \cdot C_{CH4b}} \quad (10)$$

where the effective diffusivity (D_{eff}) is estimated as $0.1D_{AB}$ (Hardiman et al., 2006), and ρ is the density of the LaFeO₃ oxygen carrier.

The all parameters that are used to evaluate the presence of diffusion limitations were listed in Table 1. The results indicate that the observed reaction rate is much smaller than the radial flux

Fig. 7. Plots obtained based on application of different gas–solid models.

of methane ($W_{\text{CH}_4\text{r}} \ll r_{\text{CH}_4\text{obs}}$), while the Weisz–Prater parameter is much smaller than 1 ($C_{\text{WP}} = 2.784 \times 10^{-5}$), which suggests that external and internal diffusion of methane are not limiting the rate of the overall reduction reaction.

3.3.2. Kinetic model

Reduction kinetics of oxygen carrier is generally used for the design of reactor, which is traditionally expected to describe the process in terms of the reaction model and of the Arrhenius parameters. Generally, an overall reaction rate is a function of solid material conversion (α), the gas-phase composition at constant feed flow rate, methane partial pressure and differential conversion (Piekiet al., 2012):

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (11)$$

The rate constant ($k(T)$) is usually assumed to obey the Arrhenius equation:

$$k(T) = A \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (12)$$

where α is the oxygen carrier conversion, t is the reduction time (s), T is the absolute temperature (K), $f(\alpha)$ is a function that represents the reaction mechanism, R is the gas constant, A and E_a are the pre-exponential factor and the activation energy, respectively. For reaction kinetics under isothermal conditions, analytically integrated to yield:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T) \cdot t \quad (13)$$

where $g(\alpha)$ is the integral form of the reaction model.

Both empirical and mechanistic models for gas–solid reaction are available in the technical literature, such as power law model, shrinking core model (SCM), nucleation and nuclei growth model (NNGM) (Adanez et al., 2012; Hossain et al., 2008; Luo et al., 2014). As mentioned above, external and internal diffusion of methane are excluded in limiting the rate of the overall reduction reaction. The kinetic-order models, contraction models (chemical reaction control) and nucleation models in Table 2 are determined to fit the reduction of LaFeO_3 data with suitable rate expressions derived from gas–solid models.

Fig. 8. Arrhenius plot used for evaluation of the activation energy of the reduction process following 2-D nucleation model.

3.3.3. Model evaluation

Hancock and Sharp developed a convenient graphical method of comparing this type of experimental data, which can be expressed in the form of the following equation to determine the reaction mechanism (Hancock and Sharp, 1972):

$$\ln [-\ln(1-\alpha)] = n \ln t + \ln \beta \quad (14)$$

where α is the oxygen carrier conversion, β is a constant which is partially dependent upon the nucleation frequency and rate of grain growth, and n is a constant associated with the geometry of the system. Presentation of this data in the specific form of the plots of $\ln [-\ln(1-\alpha)]$ against $\ln t$ are used to identify the reaction mechanism, which depend on the resulted gradient (n). If n is below 1, the reaction is in favor of a diffusion process, whereas if $1 < n < 2$, the phase boundary (or interface) control is likely to be dominant. Fig. 6 suggests that the average value of n is close to 1.5, which indicates the mechanism of phase boundary (or interface) control is likely to be dominant.

In order to apply the model-fitting method, at constant reduction temperature (T), Eq. (13) will plot as a straight line for any $g(\alpha)$ regardless of the form of that reaction mechanism [$g(\alpha)$]. The modeling results are presented in Fig. 7 and Figs. S4–6. The kinetic-order models can only be fitted well at low temperature (1073 K) in Fig. 7A, indicating that kinetic-order models cannot agree with the experimental data in the whole reductive temperature range. Fig. 7B shows that the contraction model can only fit the experimental data well at low temperatures, but it is not as good as those of the data obtained at higher temperatures of 1173 and 1223 K. Notably, the 2-D nucleation and nuclei growth model is the best suited to model the experimental results ($R^2 > 0.99$)

Fig. 9. Comparison of experimental data and fitting by 2-D nucleation model (A), Parity plots for conversion of LaFeO₃ oxygen carrier between 2-D nucleation model data and experimental data (B) at 1173 K. Symbols: experimental data. Short dot lines: model predictions from 2-D nucleation model.

(Fig. 7C). The values of kinetic rate constant (k) can be determined at different temperatures from the slope obtained by plotting $g(\alpha)$ against time, as shown in Fig. 8. The resulted apparent activation energy (E_a) is about 151 kJ/mol, while the pre-exponential factor (A) is approximately $4.53 \times 10^4 \text{ s}^{-1}$. The obtained activation

Table 3

Activation energy for CLMR reported in the literature together with the proposed 2-D nucleation model.

Oxygen carrier	Temperature range	Experimental method	Model	E_a (kJ/mol)	Reference
LaFeO ₃	1073~1223 K	Isothermal MS	2-D nucleation model	151	This work
MnFe ₂ O ₄ (Jacobsite)	1073~1173 K	Isothermal TGA	Diffusion control	139	Go et al., 2008
CeO ₂	873~1123 K	Isothermal TCD	–	137	Otsuka et al., 1999
CoWO ₄	1123~1223 K	Isothermal TGA	1st order reaction	221	Castillo et al., 2013

energy is compared with those of other studies for CLMR as shown in Table 3. The activation energy over LaFeO₃ oxygen carrier has similar value of activation energy with CeO₂ and MnFe₂O₄, and is lower than that of CoWO₄ (Otsuka et al., 1999; Go et al., 2008; Castillo et al., 2013).

3.3.4. Model validity

The validity of 2-D nucleation model for CLMR to syngas has been verified in Fig. 9A. It can be seen that the simulated values of oxygen conversion as a function of time are in good agreement with the experimental values, although there are some deviation the deviation from the experimental data for 1073 and 1123 K at long reaction time ($t > 150$ s). Root mean squared error (RMSE) and determination coefficient (R^2) are also calculated as statistical indicators to examine the adequacy of the 2-D nucleation model. The 0.0346 and 0.91 for RMSE and R^2 , respectively, also confirm a good fit for the experimental data. Furthermore, the obtained results of different cyclic number ($\alpha < 0.10$) by sequential redox reaction also verify the validity as the inset in Fig. 9B, which also show statistical indicators of 0.00399 and 0.97 for RMSE and R^2 , respectively. Therefore, the 2-D nucleation model is reasonable and reliable for CLMR to syngas. The current kinetics study by 2-D nucleation model provides a simplified approach which will help in interpreting the relationship of oxygen carrier conversion vs. time for a gas–solid reaction over fuel reactor by CLMR using LaFeO₃ as oxygen carrier, and is expected to help in the prediction, design and optimization purposes of a CLMR system.

4. Conclusion

The reduction kinetics of LaFeO₃ oxygen carrier by chemical-looping methane reforming to syngas, which characterized sigmoidal shapes, was investigated in the present work. The results from TPR, TPD, XRD SEM, TEM and XPS characterization suggest the stoichiometric relationship between oxygen carrier and methane in chemical-looping process. By applying the Hancock and Sharp method to the data, an average value of $n = 1.5$ is obtained, which indicates the phase boundary control is likely to be dominant. A wide variety of gas–solid reaction kinetics models are evaluated to determine the best fit to the experimental data, where the 2-D nucleation and nuclei growth model is used to study the kinetic parameters. The apparent activation energy is found about 151 kJ/mol, and the pre-exponential factor is about $4.53 \times 10^4 \text{ s}^{-1}$. Results obtained from this kinetic study indicate that the model performs well with the experimental conversion-time curves for the reduction of LaFeO₃ oxygen carrier in CLMR. The validity is also verified by the data from sequential redox cycles to simulate chemical-looping methane reforming process.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ces.2016.07.011>.

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