



Two-steps thermochemical cycles of H₂O/CO₂ co-splitting over Ba_{0.95}La_{0.05}FeO₃ (BLF) in a packed bed reactor and micro-channel reactor

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Abstract

Ba_{0.95}La_{0.05}FeO₃ (BLF) was synthesized using a sol–gel method. The catalytic activity of the BLF catalyst towards the co-splitting of H₂O/CO₂ was investigated in a packed bed reactor and micro-channel reactor for comparison purposes. At the maximum reduction temperature of this study (700 °C), the oxygen vacancies of 3508 μmol/g were achieved. The H₂O-TPSR and CO₂-TPSR results revealed that H₂O splitting took place at temperatures ranging from 400 to 700 °C while the CO₂ splitting occurred at temperatures higher than 600 °C. The activation energy of H₂O splitting and CO₂ splitting was calculated at 23 and 124 kJ/mol, respectively. FTIR results suggested that the active hydroxyl group was responsible for H₂O splitting, whereas the oxygen vacancy played a role in CO₂ splitting. The micro-channel reactor was found to be advantageous for only the CO₂ splitting. The hydroxyl groups were believed to be located on the catalyst's surface, while the oxygen vacancies were more likely present within the catalyst's bulk.

Keywords Micro-channel reactor · Thermochemical cycles · Perovskite · Ba_{0.95}La_{0.05}FeO₃ (BLF) · Kinetics

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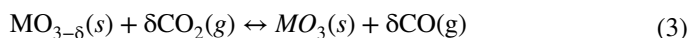
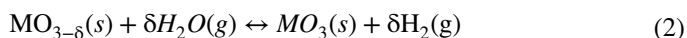
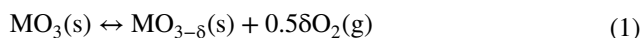
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Introduction

Energy is a critical and indispensable factor in driving the development of businesses and fostering industrial economic growth. However, the rapid consumption of fossil fuels has detrimental effects, including resource depletion and a substantial increase in global CO₂ emissions [1]. These escalating greenhouse gas emissions contribute to the intensification of global warming, which has been observed to worsen each year. Currently, researchers are actively working on reducing carbon dioxide emissions through the development of various green energy technologies. Some of these technologies include solar thermal, thermochemical processes, geothermal energy, water splitting, and onshore wind power [2]. Among these technologies, the thermochemical process stands out as an excellent method for producing green and sustainable energy without emitting any toxic gases. It offers a promising solution for addressing environmental concerns. In particular, the two-step thermochemical cycles of H₂O/CO₂ co-splitting have emerged as a crucial focus in the quest for pure syngas production [3, 4]. These cycles involve the splitting of water (H₂O) and carbon dioxide (CO₂) to generate syngas, a mixture of hydrogen (H₂) and carbon monoxide (CO). The advantage of this process is that it allows to produce syngas without the release of toxic gases, thereby contributing to a cleaner and more sustainable energy future. Given the urgency of the current environmental challenges, the development and implementation of such thermochemical cycles are deemed highly necessary. The process consists of (1) an endothermic (thermal or chemical) reduction step (700–1500 °C) that creates oxygen vacancies on the metal oxide surface (Eq. 1) and (2) an exothermic oxidation step (500–700 °C) that the reduced metal oxide is oxidized by H₂O (Eq. 2) and CO₂ (Eq. 3), producing H₂ and CO, respectively. The metal oxide is also recycled and becomes active again for the next cycles as suggested by the following Eqs. (1–3).



The changes in temperature between the reduction and oxidation steps in the two-step thermochemical cycles can result in a decrease in the overall efficiency of the process. Studies have shown that the maximal efficiency of the most sophisticated process was estimated at 10% to 30% [5, 6]. Maintaining similar reduction/oxidation temperatures or employing moderate temperatures throughout the process presents a challenge. However, despite this challenge, it is considered a suitable approach for achieving high-yield product production on an industrial scale. The industrial implementation of the thermochemical cycles involves careful consideration of process design and optimization to minimize energy losses and enhance overall efficiency. Efforts are made to mitigate the negative impact of temperature changes between the steps through advanced reactor design, heat integration, and thermal management strategies. By addressing these challenges and optimizing the process

parameters, it becomes feasible to achieve higher yields and improve the overall efficiency of the two-step thermochemical cycles. There is also a rising interest in developing low-cost, earth-abundant, eco-friendly, and low-temperature reduction catalysts for $\text{H}_2\text{O}/\text{CO}_2$ co-splitting reactions [7]. The goal is to find catalyst materials that are affordable, readily available, and environmentally friendly, while still maintaining high efficiency in the co-splitting process.

Perovskite materials are particularly attractive for these applications due to their unique properties. Perovskites possess high oxygen vacancies and excellent oxygen mobility, making them well-suited for redox reactions involved in co-splitting processes. They also exhibit good stability and have a long lifespan, which is advantageous for continuous operation. Furthermore, perovskites are known for their low cost compared to noble metal catalysts, making them a practical choice for large-scale industrial applications. Perovskite materials have already demonstrated their potential in various energy-related applications, such as fuel cells [8], electrochemical cells [9], and thermochemical splitting redox reactions [6, 7]. Their versatility and desirable properties make them promising candidates for $\text{H}_2\text{O}/\text{CO}_2$ co-splitting reactions, offering a pathway towards efficient and sustainable production of hydrogen and carbon monoxide. Continued research and development efforts in perovskite catalysts hold the potential to advance the field of co-splitting and contribute to the transition towards a cleaner and greener energy future.

Compared to $\text{CeO}_2/\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$, perovskites such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [10, 11], $\text{Sr}_{1-x}\text{La}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ [12], and $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ [13] have shown favorable H_2/CO production [14]. Specifically, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) [15], exhibited outstanding catalytic performance (relatively lower operation temperatures with higher yield H_2 production). Both BSCF and LSCF were reported to provide significant degree of oxygen deficiency and high oxygen surface exchange rate [12, 13, 16]. It was reported previously that the highest oxygen permeation, associated with the oxygen storage capacity (OSC), is obtained when the percentage of La is at 5% [17]. Ultimately, these factors contribute to reducing the reduction/oxidation temperature and improving the catalytic performance of $\text{H}_2\text{O}/\text{CO}_2$ splitting cycles. However, BSCF and LSCF may exhibit lower H_2 production in the second cycle. This can be attributed to the extraction of cobalt through the reduction of cobalt cation, which can result in instability at high temperatures [15, 18–20]. To tackle this issue, there has been a renewed interest in the development of cobalt-free perovskite materials that can operate in long-term continuous production for similar applications. $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$ (BLF) perovskite, known for its exceptional catalytic performance, provides an alternative to cobalt-based perovskite materials. It offers high oxygen permeation flux and significant oxygen deficiency, reaching values of $3.2 \text{ ml}/\text{cm}^2/\text{min}$ and $\delta=0.3$ [17, 21]. In our previous study, BLF has been successfully utilized in thermochemical water splitting within a packed bed reactor, demonstrating higher H_2 production compared to BaFeO_3 (BF) and $\text{BaFe}_{0.975}\text{Gd}_{0.025}\text{O}_3$ (BFG) [22]. Scaling up packed-bed reactors to pilot or commercial scale can be challenging due to their large size. The size of the reactor can make it more difficult to adjust operating conditions, especially during the required two-step operations. As an alternative choice, microchannel reactors offer several advantages. They have

a high surface-to-volume ratio, negligible pressure drops, and excellent mass/heat transfer capabilities [23, 24]. These features make microchannel reactors an interesting option for overcoming the challenges associated with scaling up and optimizing the operation of thermochemical processes. In this study, the potential of $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$ (BLF) for high-purity syngas production via $\text{H}_2\text{O}/\text{CO}_2$ thermochemical splitting cycles was investigated using both a microchannel reactor and a packed bed reactor. The physical and chemical properties of BLF were characterized using XRD, H_2 -TPR, H_2O -TPSR, CO_2 -TPSR, and FT-IR techniques to examine the crystal structure, oxygen release behavior, oxygen uptake behavior in the presence of H_2O and CO_2 on the BLF surface, and surface adsorption on BLF. Furthermore, the H_2/CO production in the microchannel reactor and packed bed reactor was compared, focusing on the effect of reduction/oxidation temperature. The kinetics parameters, including activation energy and pre-exponential factor, were estimated using the Boltzmann equation to gain further insights into the reaction kinetics.

Experimental

Catalyst's Preparation

BLF was synthesized using the sol–gel method. The catalyst's precursors, namely 5.15 g of $\text{Ba}(\text{NO}_3)_2$ (Carlo Erba, 99%), 0.45 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Himedia, 99%), and 8.37 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Ajax Finechem, 98%), were dissolved in 100 mL of deionized water. Simultaneously, 12.11 g of ethylenediaminetetraacetic acid (EDTA, Ajax Finechem, 99.4%) was dissolved in 2 M NH_4OH (J.T. Baker, 28–30%). The $\text{EDTA-NH}_4\text{OH}$ solution was added dropwise to the metal nitrate solution. To adjust the pH to 6, a mixture of 13.06 g of citric acid (CA, Lobachemie, 99.5%) and 2.31 mL of ethylene glycol (EG, Ajax finechem) was added. The molar ratio of metal:CA:EDTA:EG was maintained at 1:1.5:1:1. The mixed solution was continuously stirred at 90 °C for 2 h. and subsequently dried overnight at 100 °C. The resulting solid residues were crushed and subjected to calcination through the following steps: (1) heating at 325 °C for 6 h, (2) heating at 400 °C for 2 h, (3) heating at 600 °C for 8 h, and (4) heating at 900 °C for 12 h with a heating rate of 2 °C/min.

Preparation of Suspension Solution for Wash Coating

Polyvinyl alcohol ($(\text{C}_2\text{H}_4\text{O})_x$, Chem-supply) was dissolved in deionized water at the weight ratio of 84 to 5. The process took place at a temperature of 65 °C while continuously stirring the solution for a duration of 3 h. The solution was left overnight before the previously synthesized catalyst and acetic acid were added into. The resulting solution was again stirred for 3 h at 65 °C before cooled down to room temperature while stirred for an additional 72 h. The solution was wash-coated on

the stainless-steel micro-channel plates which was reported previously [25]. The coated substrates were calcined at 500 °C for 3 h. with the heating rate of 1 °C /min.

Characterization

The crystal structure of BLF was investigated by XRD (Cu K_{α} as X-ray source, wavelength 1.5418 Å) with the scanning rate of 5°/min (Rigaku TTRAX III model). The hydrogen temperature programmed reduction (H_2 -TPR), H_2O temperature programmed surface reaction (H_2O -TPSR), and CO_2 temperature programmed surface reaction (CO_2 -TPSR) were implemented to measure the catalyst's in-situ characteristics such as amount oxygen releasing, reducibility, H_2 production, and CO production. 1 g of BLF was packed in a quartz tube packed bed reactor (internal diameter of 10 mm, diameter of 13 mm, 25 cm length), at temperature range of 100–950 °C with heating rate of 5 °C/min using an electrical furnace. Prior the tests, the catalyst was activated using 10% H_2 /Ar at 700 °C with total flow rate of 200 mL/min. The surface functional groups of BLF were also studied by FT-IR spectroscopy (Perkin Elmer, Spectrum2000) with the wavelength 400–4000 cm^{-1} during H_2O / CO_2 co-splitting reaction. The specific probe gas, H_2 , H_2O , and CO_2 , was introduced individually during such tests.

Reactivity Study

The catalytic performance of the catalyst was tested and compared using both a packed-bed reactor and a microchannel reactor. The specific details of each reactor setup are provided in Table 1. The packed-bed reactor used in the catalytic performance testing was the same reactor employed in the probe reaction test. On the other hand, the microchannel reactor used in the study was constructed by Thai German Institute (TGI, Thailand) using 316 L stainless steel [26]. Both reactors were placed in the testing rig shown in Fig. 1. For all experiments, the molar ratio of feed reactants (H_2O/CO_2) was fixed at 1:1 with the total flow rate of 200 mL/min. The reduction and oxidation time was 30 and 15 min. The operating temperature of reduction and oxidation steps were varied from 500 to 700 °C. After the reaction, the gaseous products were collected every single minute using gas bags, before

Table 1 The details of microchannel and packed bed reactor

	PBR	MCR
Material	Quartz	316 L stainless steel
Reactor size	10 mm ID	14 channels
	13 mm OD	370 μm width
	25 cm length	330 μm depth
		50 mm length
Weight of BLF per reactor	0.5 g	0.1 g
WHSV	24,000 mL/g/h	120,000 mL/g/h

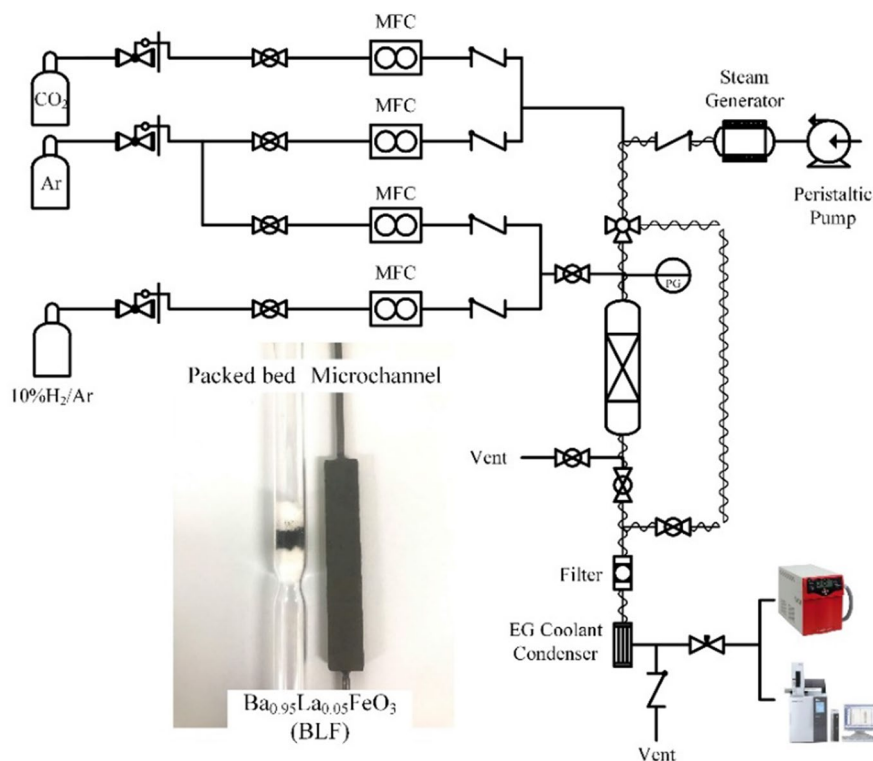


Fig. 1 Rig diagram for all the experiments

analyzed by a gas chromatography (Shimadzu GC-2014ATP, TCD/FID detectors). The kinetic parameters were determined using the Boltzmann model (Eq. 4)

$$X(t) = X_u - \frac{X_u}{1 + \exp \left[\frac{(t-t_0)k'}{X_u} \right]} \quad (4)$$

Result and Discussion

Characterization

The Crystal Structure of BLF by XRD

Since the catalyst needs to be reduced before the reaction, an XRD analysis was conducted to verify that the crystallinity of the BLF remains unchanged after the reduction process. Fig. 2a and b depict the XRD patterns of the BLF before and

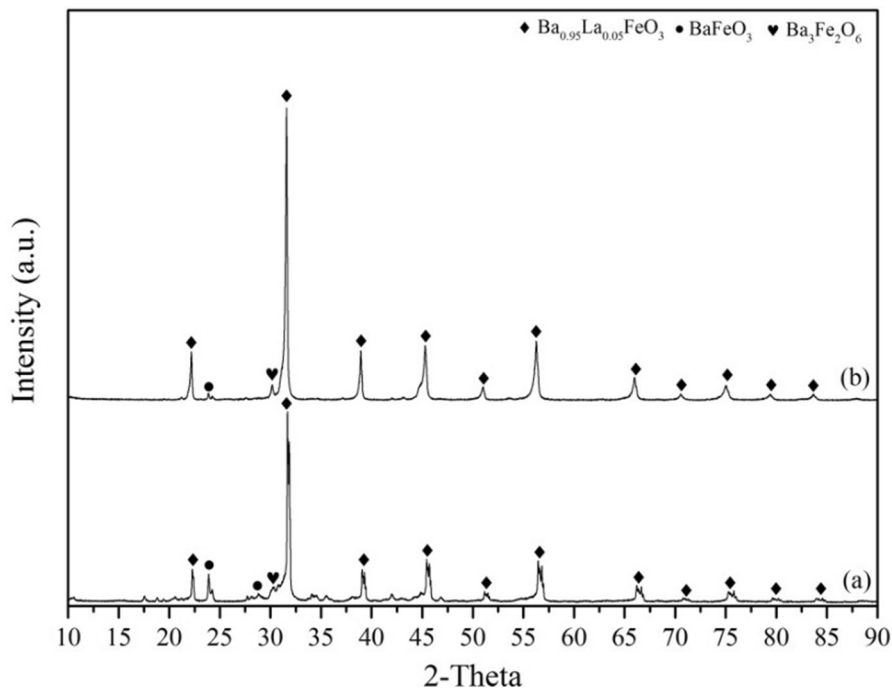


Fig. 2 Diffractogram of the synthesized BLF using sol–gel method comparing between (a) BLF before reduction using 10% H_2 /Ar at 700 °C and (b) BLF after the reduction

after the reduction process using 10% H_2 /Ar at 700 °C. Both samples share the major crystalline phase of the desired $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$ with the minor crystalline phases of $\text{Ba}_3\text{Fe}_2\text{O}_6$ (PDF Card No. 00-023-1023). However, a notable change occurred in the XRD patterns after the reduction process. The peak corresponding to BaFeO_3 (PDF Card No. 01-075-0276) disappeared in Fig. 2b. This suggests that the reduction process led to the conversion of BaFeO_3 into $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$, resulting in the disappearance of the former phase. Based on these results, it can be concluded that the BLF catalyst maintained its stable cubic perovskite phase after the reduction process, as evidenced by the presence of the desired crystalline phase ($\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$, BLF) and the absence of BaFeO_3 .

Temperature Programmed Probe Reactions

H_2 -TPR (Hydrogen Temperature-Programmed Reduction) The temperature-dependent redox behavior of BLF was investigated using H_2 -TPR. During the reduction process, the oxidation state of iron (Fe) underwent a change from Fe^{4+} to Fe^{3+} and from Fe^{3+} to Fe^{2+} at a temperature of 525 °C giving oxygen release of 2194 $\mu\text{mol/g}$. Whereas the reduction of Fe^{2+} to Fe^0 took place at 850 °C and 950 °C, the sum of oxygen vacancy at this stage was calculated at 2776 $\mu\text{mol/g}$ (Fig. 3).

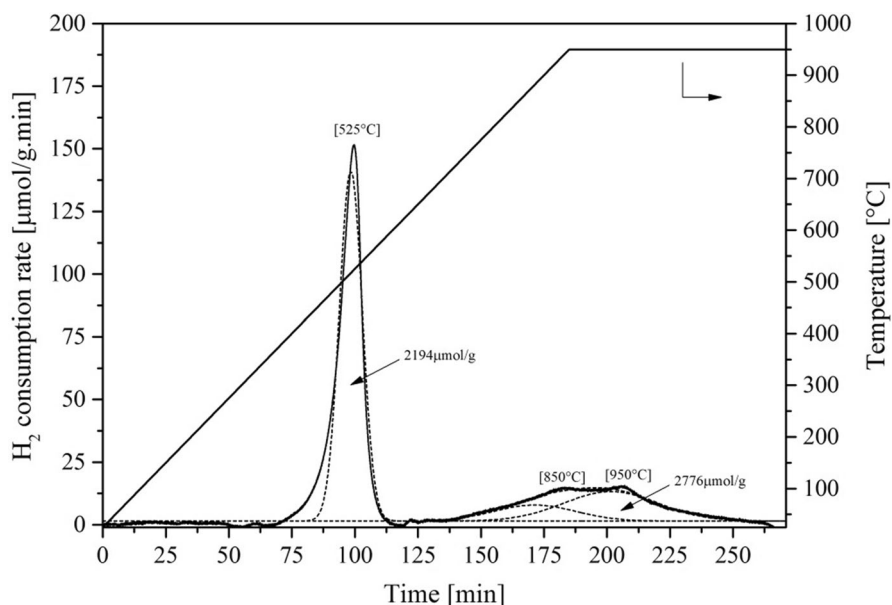


Fig. 3 H_2 -TPR profile of BLF

H_2O -TPSR and CO_2 -TPSR (H_2O Temperature-Programmed Surface Reaction and CO_2 Temperature-Programmed Surface Reaction) The oxidation of H_2O and CO_2 at the surface of BLF was examined individually across a temperature range of 100 to 900 °C. These investigations are depicted in Fig. 4a for H_2O splitting (H_2 production) and Fig. 4b for CO_2 splitting (CO production). The figure illustrates H_2 and CO productions as a function of temperature. H_2O splitting was observed at 500 to 550 °C giving H_2 production of 3336 $\mu\text{mol/g}$ ($\delta=0.477$) (equivalent to 95% of solid conversion). CO_2 splitting on the other hand occurred at higher temperatures, 650 to 950 °C, giving CO production measured at 2740 $\mu\text{mol/g}$ ($\delta=0.395$) (78% of solid conversion) and 724 $\mu\text{mol/g}$ ($\delta=0.104$) (20% of solid conversion). The second peak of CO_2 splitting (at 950 °C) indicated that the lattice oxygen could diffuse from bulk to surface at this temperature range.

Surface Absorption on BLF by FT-IR Technique FT-IR spectra of the BLF which was fresh, activated (by H_2/Ar at 700 °C), oxidized by H_2O and oxidized by CO_2 were shown in Fig. 5a–d. Four major vibrational peaks appeared at $\sim 3400\text{ cm}^{-1}$ (O–H stretching), $\sim 1450\text{ cm}^{-1}$ and $\sim 850\text{ cm}^{-1}$ (carbonate) and $\sim 600\text{ cm}^{-1}$ (M–O stretching). The activated catalyst (Fig. 5b) showed more obvious O–H stretching compared to the fresh catalyst (Fig. 5a), suggesting that reduction process encouraged the formation of the active hydroxyl group, where the hydrogen could originate from either vapour (thermal reduction) or reducing hydrogen (chemical reduction). The catalyst which was oxidized by H_2O (Fig. 5c) showed disappearance of the O–H stretching, implying that the hydroxyl group is an active site for H_2O splitting. Spillover effect, or the hydrogen spillover, is suggested to be responsible for less intensity of the M–O

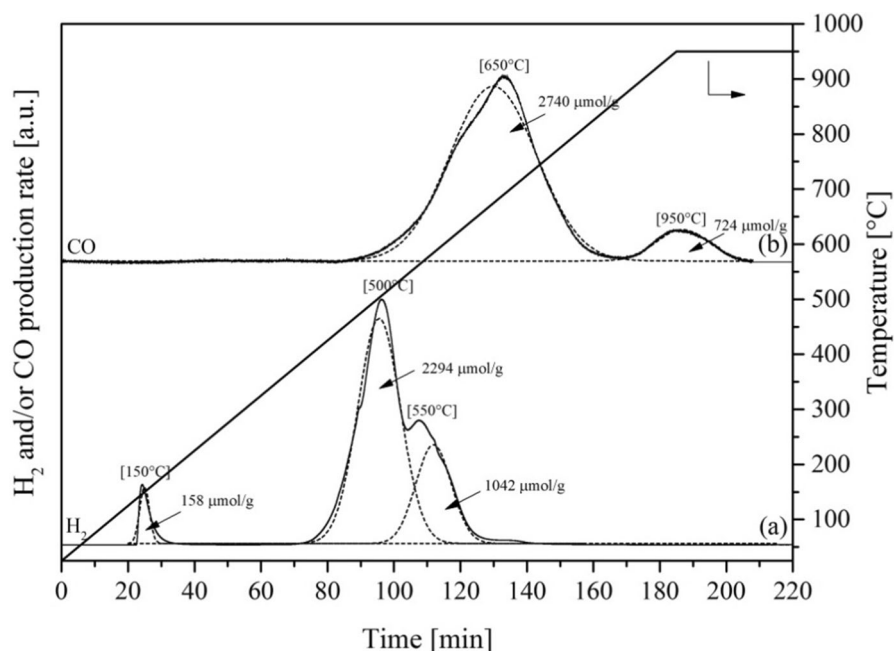


Fig. 4 TPSR profile of BLF using (a) H_2O and (b) CO_2 as a reactant

stretching (Fig. 5c). On the other hand, CO_2 splitting does not seem to affect the intensity of the O–H stretching or the M–O stretching (comparing between Fig. 5b and d). Therefore, the oxygen vacancy in the perovskite could act as an active site for the CO_2 splitting. The pronounced carbonate functional group detected in Fig. 5d was found to remain on the surface (post-exposure in CO_2 stream at 700 °C), due to high adsorption energy of surface CO_2 . This adsorbed species could cause the active site's blockage [27], resulting in a drop of product yield. The TPSR profile (Fig. 4b) showed that at temperature of 950 °C, the CO started to be released again and possible the catalyst's active site became unblock at such temperature.

The Effect of Temperatures on BLF Reactivity

Fig. 6 depicts the production of H_2 and CO through the co-splitting of H_2O and CO_2 at various temperature conditions. The oxidation temperature was maintained at a constant value of 700 °C, while the reduction temperature varied between 500 and 700 °C. The findings indicated that the number of oxygen vacancies increased with higher reduction temperatures. The maximum oxygen vacancy of 3508 $\mu\text{mol/g}$ ($\delta=0.5$) was achieved at the oxidation temperature of 700 °C. The production yield was predominantly influenced by the presence of oxygen vacancies. However, there was no significant difference in the production yields when the reduction

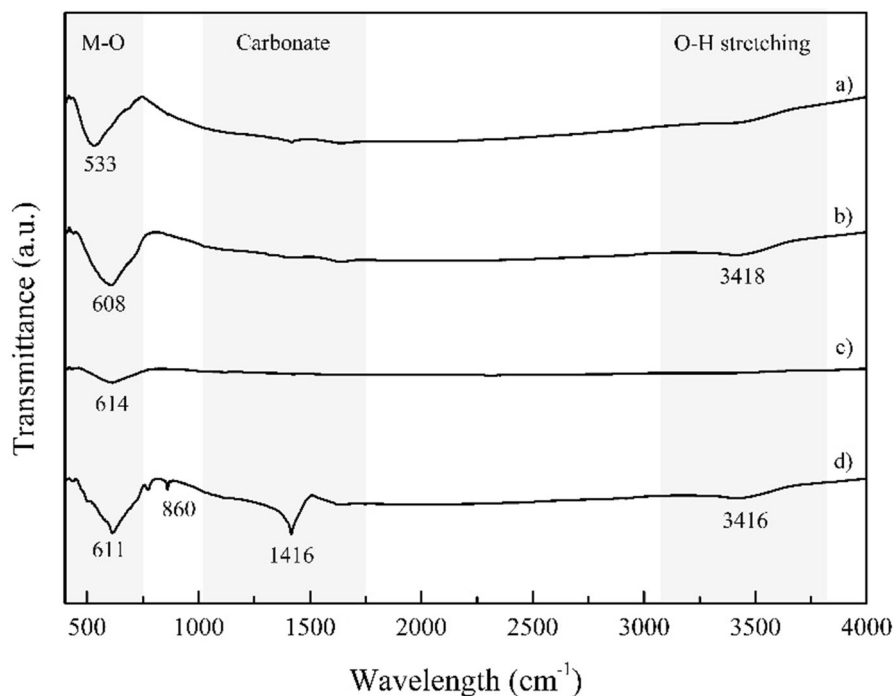


Fig. 5 FT-IR spectra of surface functional group on the (a) fresh BLF, (b) activated BLF under H_2 at 700 °C, (c) BLF oxidized by H_2O and (d) BLF oxidized by CO_2 at 700 °C

temperature was set at either 600 or 700 °C, as they were limited by the oxidation temperature of 700 °C. Considering the excessive number of oxygen vacancies ($3508 \mu\text{mol/g}$) ($\delta=0.5$) at reduction temperature of 700 °C, it can be inferred that the surface coverage was not fully utilized at this condition. Considering the FTIR results (Fig. 5) indicating that H_2 production occurs on the active hydroxyl groups, it is unlikely that an increased number of oxygen vacancies would enhance H_2 production. In this case, the presence of active hydroxyl groups, rather than oxygen vacancies, would be the primary factor influencing H_2 production. On the other hand, it is hypothesized that the production yield of CO may increase when the oxidation temperature exceeds 700 °C. In addition, it was observed that the micro-channel reactor enhanced CO production but had an unclear impact on H_2 production.

Fig. 7 shows the effect of oxidation temperature which was varied from 500 to 700 °C, while the reduction temperature was fixed at 700 °C for all experiments. It was observed that the H_2O splitting could occur at oxidation temperatures as low as 500 °C. The result corresponded with H_2O -TPSR reported in Fig. 4a, which indicated that the splitting of H_2O could nearly reach completion at temperatures below 600 °C, with an estimated solid conversion rate of 95%. For the packed-bed reactor, the production of H_2 and CO were found to be sensitive to the rise of oxidation temperatures. For the micro-channel reactor, an increase

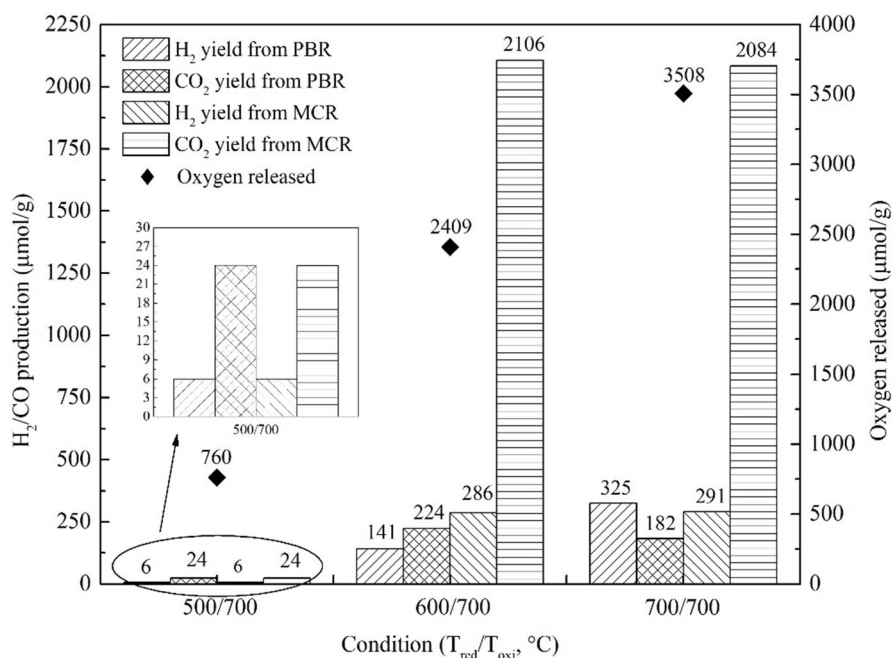


Fig. 6 The effect of reduction temperatures on the catalytic performance of BLF towards H₂O/CO₂ co-splitting in a packed-bed and micro-channel reactor. For all the experiments, the molar feed ratio of H₂O:CO₂ was 1:1; total volumetric flowrate was 200 mL/min; the reduction and oxidation time was fixed at 30 and 15 min; the catalyst's weight for PBR and MCR was 0.5 and 0.1 g; WHSV for PBR and MCR was at 24,000 and 120,000 mL/g/h

in the oxidation temperature highly influenced the production of CO, but not that of H₂. Because the H₂O and CO₂ splitting reactions were exothermic, the CO production was therefore limited by its kinetics and not likely the number of its active sites, whereas the H₂ production was controlled by the limited number of active hydroxyls. It can be concluded that the micro-channel reactor is more advantageous for CO splitting compared to H₂O splitting, particularly at oxidation temperatures exceeding 650 °C. The reactor demonstrated a significant increase in CO production with rising oxidation temperatures, indicating its effectiveness in facilitating the CO splitting reaction. However, the H₂O splitting process did not show a similar level of improvement, suggesting that the micro-channel reactor may not be as favorable for H₂O splitting at higher oxidation temperatures.

Fig. 8 presents the productivity of H₂ and CO when the reduction and oxidation temperature was kept the same at 500/500, 600/600, and 700/700 °C. The result followed the same trends as reported earlier in Figs. 6 and 7. The solid conversion was calculated at 0, 46 and 68%. The optimal pair of reduction/oxidation temperature for the packed-bed reactor and micro-channel reactor was 600/600 °C. Table 2 compared the catalysts from this work with others. It

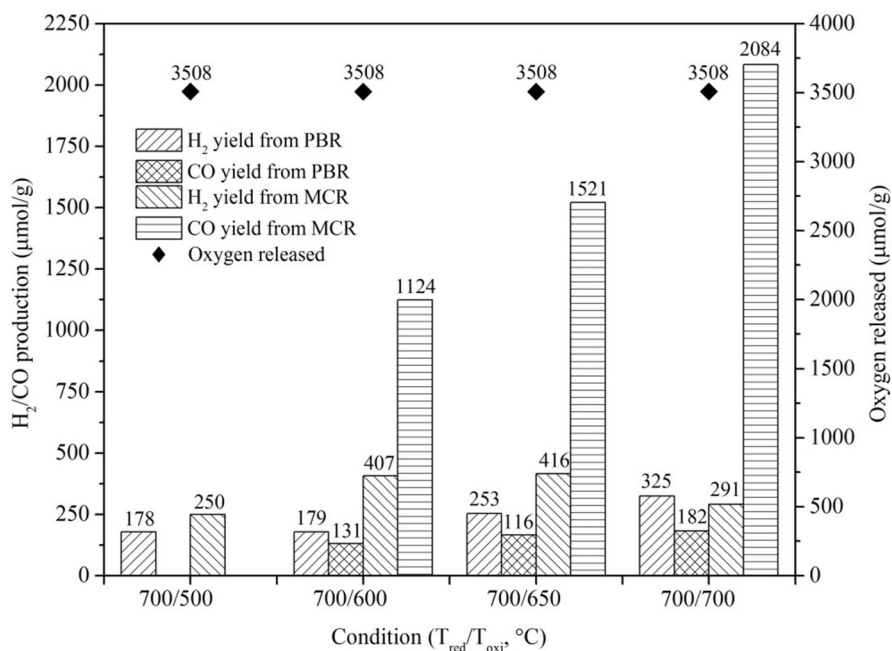


Fig. 7 The effect of oxidation temperatures on the catalytic performance of BLF towards H₂O/CO₂ co-splitting in a packed-bed and micro-channel reactor. For all the experiments, the molar feed ratio of H₂O:CO₂ was 1:1; total volumetric flowrate was 200 mL/min; the reduction and oxidation time was fixed at 30 and 15 min; the catalyst's weight for PBR and MCR was 0.5 and 0.1 g; WHSV for PBR and MCR was at 24,000 and 120,000 mL/g/h

was found that the catalysts from this work can perform at significantly lower temperature range and still offer one of the best productivities.

Kinetics Analysis

Boltzmann plot was applied to evaluate the activation energy and the pre-exponential factor of the rate equations, as shown in Figs. 9 and 10. The activation energy of H₂O splitting and CO₂ splitting was estimated at 23.17 kJ/mol and 123.99 kJ/mol. Their pre-exponential factors are 0.03 s⁻¹ and 49,137.88 s⁻¹.

Conclusion

The synthesized BLF exhibited a cubic structure. The thermal stability of the perovskite is typically influenced by its crystal structure, although it is not solely determined by it. Other significant factors, including the ionic radius ratio, tolerance factor, and composition, also contribute to the perovskite's thermal stability. Therefore, further study on the impact of these factors should

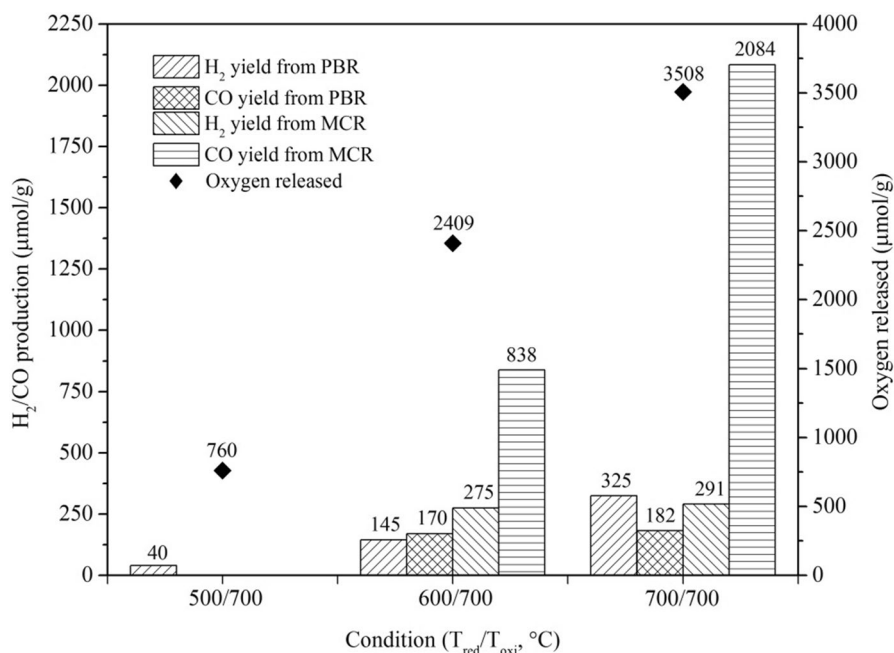


Fig. 8 Syngas productivity over the BLF when the reduction and oxidation temperatures are equally paired at 500/500 °C, 600/600 °C, and 700/700 °C. For all the experiments, the molar feed ratio of H₂O:CO₂ was 1:1; total volumetric flowrate was 200 mL/min; the reduction and oxidation time was fixed at 30 and 15 min; the catalyst's weight for PBR and MCR was 0.5 and 0.1 g, WHSV for PBR and MCR was at 24,000 and 120,000 mL/g/h

Table 2 Comparison between the catalyst in this study and other studies

Oxygen carrier materials	Temperature (°C) (red/ox)	Reducer	Oxidizer	Production (μmol/g)		Total production (μmol/g)
				H ₂	CO	
Ce _{0.8} Zr _{0.2} O _{2-δ} [28]	825/825 ^a	H ₂	H ₂ O	1530	—	1530
CeO _{2-δ} [28]	825/825 ^a	H ₂	H ₂ O	1240	—	1240
Ce _{0.5} Zr _{0.5} O _{2-δ} [29]	900/900 ^a	H ₂	H ₂ O	1150	—	1150
Ce _{0.75} Zr _{0.25} O _{2-δ} [30]	900/900 ^a	H ₂	H ₂ O	1694	—	1694
CeO _{2-δ} [31]	700/700 ^a	H ₂	H ₂ O	260	—	260
Ce _{0.7} Zr _{0.3} O _{2-δ} [32]	850/700 ^a	CH ₄	H ₂ O	1580	—	1580
CuFe ₂ O ₄ /ZrO ₂ [33]	900/800 ^a	CH ₄	H ₂ O	2780	—	2780
BaFeO _{3-δ} [22]	900/900 ^a	H ₂	H ₂ O	1200	—	1200
Ba _{0.95} La _{0.05} FeO _{3-δ} [22]	900/900 ^a	H ₂	H ₂ O	1310	—	1310
La _{0.3} Sr _{0.7} Co _{0.7} Fe _{0.3} O _{3-δ} [34]	700/700 ^a	H ₂	H ₂ O/CO ₂	2266	705	2971
Ba _{0.95} La _{0.05} FeO _{3-δ}	700/700 ^b	H ₂	H ₂ O/CO ₂	2084	291	2375
(This study)	700/700 ^a	H ₂	H ₂ O/CO ₂	325	128	453

^aPerformed in PBR

^bIn MCR

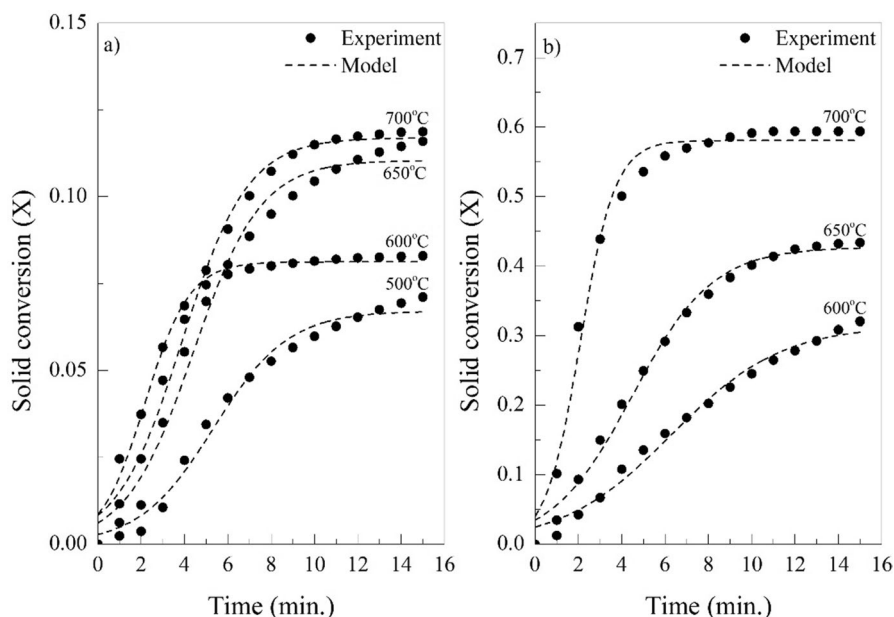


Fig. 9 Solid conversions of BLF, in the MCR, compared between experimental and modelled for **a** H₂O splitting to H₂ **b** CO₂ splitting to CO at temperatures varied from 500, 600, 650, and 700 °C. For all the experiments, the molar feed ratio of H₂O:CO₂ was 1:1; total volumetric flowrate was 200 mL/min; the oxidation time was 15 min; the catalyst's weight was 0.1 g; WHSV was 120,000 mL/g/h

be researched. The H₂O splitting and CO₂ splitting were believed to occur on the different types of active site. While H₂O splitting was suggested to take place on the active hydroxyl groups, CO₂ splitting was likely to happen on the oxygen vacancies. Within the studied temperature range, BLF is more selective for CO₂ splitting than H₂O splitting. In this study, the H₂ production seemed to be governed by the number of its active site, whereas the CO production was possibly kinetically limited as its productivity was continuously increasing with an increase of oxidation temperatures, despite being exothermic. The micro-channel reactor has advantages over the packed-bed reactor for CO production, but not H₂ production. The result suggested various possibilities such as (1) the active hydroxyl group (responsible to split H₂O) are mostly located at the surface of the catalyst (2) the oxygen vacancies (active sites for CO₂ splitting) are mainly located within the catalyst's bulk (3) the number of hydroxyl group is relatively a lot less than the number of oxygen vacancies (per weight of the catalyst) and (4) the reaction rate of H₂O splitting is relatively faster than that of the CO₂ splitting. The activation energy of H₂O splitting in MCR ($E_a = 23.17$ kJ/mol) is significantly lower than that in PBR (47.4 kJ/mol), reported by our previous research [22]. To validate these hypotheses, a more in-depth investigation into the catalyst's surface area, surface mechanism and porosity is warranted.

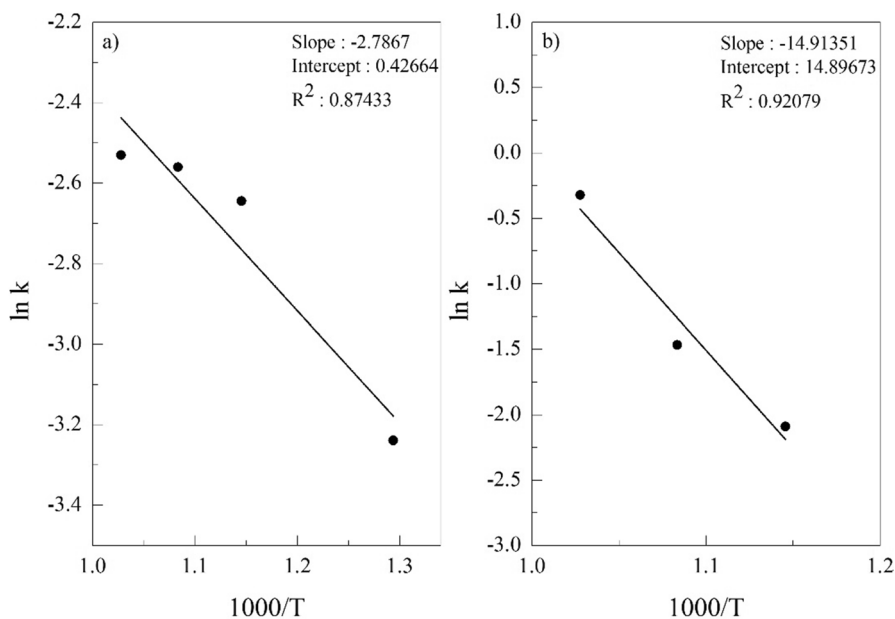


Fig. 10 Arrhenius plots of BLF for **a** H_2O splitting to H_2 **b** CO_2 splitting to CO at temperatures varied from 500, 600, 650, and 700 °C, in the MCR. For all the experiments, the molar feed ratio of $\text{H}_2\text{O}:\text{CO}_2$ was 1:1; total volumetric flowrate was 200 mL/min; the oxidation time was 15 min; the catalyst's weight was 0.1 g; WHSV was 120,000 mL/g/h

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