Isothermal Splitting of CO_2 to CO Using Cobalt-Ferrite Redox Looping

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Rising atmospheric CO_2 levels from significant imbalance between carbon emissions from fossil fuel utilization, especially for energy and chemicals, and natural carbon sequestration rates is known to drive-up the global temperatures and associated catastrophic climate changes, such as rising mean sea level, glacial melting, and extinction of ecosystems. Carbon capture and utilization techniques are necessary for transition from fossil fuel infrastructure to renewable energy resources to help delay the dangers of reaching to the point of positive feedback between carbon emissions and climate change which can drive terrestrial conditions to uninhabitable levels. CO_2 captured from the atmosphere directly or from flue gases of a power plant can be recycled and transformed to CO and syngas for use as energy and value-added chemicals. Utilizing renewable energy resources to drive CO_2 conversion to CO via thermochemical redox looping can provide a carbon negative renewable energy conversion pathway for sustainable energy production as well as value-added products. Substituted ferrites such as Co-ferrite, Mn-ferrite were found to be promising materials to aid the conversion of CO_2 to CO at lower reduction temperatures. Furthermore, the conversion of these materials in the presence of Al_2O_3 provided hercynite cycling, which further lowered the reduction temperature. In this paper, Co-ferrite and Co-ferrite-alumina prepared via co-precipitation were investigated to understand their potential as oxygen carriers for CO_2 conversion under isothermal redox looping. Isothermal reduction looping provided improved feasibility in redox conversion since it avoids the need for temperature swinging which improves thermal efficiency. These efforts alleviate the energy losses in heat recovery while also reducing thermal stresses on both the materials and the reactor. Lab-scale testing was carried out at 1673 K on these materials for extended periods and multiple cycles to gain insights into cyclic performance and the feasibility of sintering, which is a common issue in iron oxide-based oxygen carriers. Cobalt doping provided with lowering of reduction temperature requirement at the cost of oxidation thermodynamic spontaneity that required increased oxidation temperature. At the concentrations examined, these opposing phenomena made isothermal redox operation feasible by providing high CO yields comparable with oxygen carriers in the literature, which were operated at different temperatures for reduction and oxidation. Significantly high CO yields ($\sim$750 μmol/g) were obtained from Co-ferrite isothermal redox looping. Co-ferrite-alumina provided lower CO yields compared with Co-ferrite. The oxygen storage was similar to those reported in the literature on isothermal H_2O splitting, but with improved morphological stability at high temperature, especially compared with ferrite. This pathway of oxygen carrier development is considered suitable with further requirement in optimization for scaling of renewable CO_2 conversion into valuable products. [DOI: 10.1115/1.4048077]

Keywords: air emissions from fossil fuel combustion, alternative energy sources, energy extraction of energy from its natural resource, renewable energy, unconventional petroleum

Introduction

Anthropogenic carbon emissions continue to disrupt the carbon cycle leading to unwanted anthropogenic impact on the feedback between carbon cycle and the global inhabitability parameters such as temperature, mean sea level, and ocean acidity. While CO_2 emissions from anthropogenic activities have increased to 37 Gton/yr (global energy related CO_2 in 2017) [1], natural carbon sinks such as ocean and biosphere are expected to reach their saturation limit which will result in acceleration of climate change [2]. Continuously increasing fossil fuel consumption is the main reason for these unprecedented carbon emissions followed by deforestation. Energy and value-added chemicals are the commodities in demand that links to fossil fuel consumption [3]. Transition away

from fossil fuels and toward renewable energy resources such as solar, biomass, wind, and geothermal energies provides mitigation from future carbon emissions. Realization of the future of fully renewable energy infrastructure assumes the time scale for catastrophic climatic activities to be later compared with this infrastructure time. But the climate models could include significant underestimation of the climate change and current atmospheric carbon content and additional carbon emissions that would be released from now until all renewables in the future. This alone could have disastrous effects on the global temperature and inhabitability of our planet. This potential risk calls for carbon capture and active sequestration, and utilization in parallel with efforts on renewable energy to effectively seek carbon negative pathway for the near future. The demand for carbon based energy, value-added chemicals, the need for renewable energy utilization and the necessity for CO_2 utilization can all be addressed together via solar-thermochemical conversion of CO_2 and H_2O into syngas (CO and H_2) which can then be utilized for various applications including carbon energy and chemicals production [4,5].

Thermochemical redox looping of metal oxides and mixed metal oxides at high temperature has been the most preferred pathway for CO_2 conversion as it requires only two steps and avoids the use of corrosive chemicals present in other thermochemical (CO_2/H_2O) conversion cycles [6,7]. These metal oxides are referred to as oxygen carriers (OC) and are classified into volatile and non-volatile cycles. The volatile cycles involve oxygen carriers with boiling point lower than operational temperatures such as ZnO/Zn, SnO/Sn while non-volatile cycles include solid oxygen carriers with no phase change during the cycles such as CeO_2, Fe_3O_4, and perovskites [8]. While volatile cycles provide thermodynamic advantage with higher spontaneity, the practicality of handling metal vapors and the need for rapid quenching makes them unattractive. Non-volatile cycles have been the most studied thermochemical redox cycles for CO_2 and H_2O splitting [8,9].

CeO_2 and its doped derivatives have been the most researched class of materials as oxygen carriers due to their significantly fast redox kinetics and high-temperature resiliency, and thus sustained cycle performance. But these materials typically require reduction temperature as high 1800 K along with significant requirement of low partial pressures of O_2 for comparable oxygen storage capacity [10]. Iron oxide-based materials were also proposed of which substituted ferrite-based materials were found to provide higher performance in terms of lowered reduction temperature and higher oxygen storage capacity [11–16].

Substituted ferrites are typically of the form $M_xFe_{3-x}O_4$. Different metals were studied at the substituent M to form a spinel structure. Co, Ni, Mn, Zn, and Fe are the most chosen substituents as they provided better thermodynamics by lowering the required reduction temperature, albeit at the cost of lowering spontaneity in their oxidation steps [8]. Co and Mn were found to show this behavior according to thermodynamic and experimental studies into Co and Mn ferrites especially for H_2O splitting [8,17]. Similar to other iron oxide-based materials, these ferrites were found to be prone to high-temperature sintering which lowered their cycle performance from the loss of active surface area. To avoid this, ferrite deposition on high-temperature resilient substrates such as ZrO_2, Al_2O_3, and yttrium stabilized zirconia (YSZ) were proposed and these studies showed formation of solid solution of Fe^{2+} with the substrate during thermal reduction and thus providing structural stability [8,12,15,18–20]. In the case of Al_2O_3, thermal reduction of $M_xFe_{3-x}O_4$ with Al_2O_3 led to the formation of aluminates and reduction of Fe^{3+} to Fe^{2+} and thus releasing O_2. The thermodynamic stability of these aluminates improved the spontaneity of reduction step and thus allowing for thermal reduction at relatively low temperatures compared with ferrites. These aluminate-based ferrite cycles are referred to as hercynite cycles in the literature due to the formation of hercynite intermediates. The improvement of reduction thermodynamics by incorporating Co ions and addition of Al_2O_3 substrates comes at the cost of lowered spontaneity in oxidation step where CO_2 reacts with the reduced state oxygen carrier to oxidize them and thus evolve CO. This resulted in the investigation into different compositions of substitution and alumina content so as to balance the advantages in reduction step with the disadvantages in oxidation step [8].

Typical ferrite-based redox cycling involves reduction at high temperature 1600–1800 K in inert gas to produce O_2 followed by oxidation step at lower temperature (1100–1400 K), as in CO_2/H_2O conversion to CO/H_2. The reduction step is repeated to regenerate the lower oxidation state oxygen carrier to further repeat these cycles. While temperature swinging was the most studied pathway for redox looping, isothermal operation has also been investigated by cycling between inert gas and high CO_2 content input gas [21]. Thermodynamic studies on isothermal and temperature swinging operation revealed that while temperature swinging provided higher maximum solar-to-fuel efficiency, isothermal operation provides alleviation of complex solid–solid heat recovery, and thermal fatigue in the oxygen carrier and reactor materials and provides higher throughput via lower latency due to heating and cooling. Although required inert gas for isothermal operation is higher than

temperature swinging, development of high-temperature oxygen separation, and improved design for gas–gas heat recuperation make isothermal operation preferable to temperature swinging [22].

Isothermal redox looping of hercynite cycle using $CoFe_2O_4.3Al_2O_3$ for H_2O splitting at 1623 K was demonstrated to reveal that it produced H_2 more than thrice compared with hercynite cycling from temperature swinging and almost 12 times compared with CeO_2 cycling from 1632 K to 1273 K [23]. This study provided the evidence on feasibility of isothermal operation and its higher yield without the need for temperature swinging. While isothermal redox looping has been studied for H_2O splitting, hercynite, and ferrite cycle conversion and its feasibility in isothermal redox looping is lacking in the current literature. The present paper addresses such lack of information into the feasibility study of CO_2 splitting in isothermal redox looping using ferrite spinel oxygen carriers and hercynite cycle. Cobalt-substituted ferrite and its equivalent hercynite were prepared via co-precipitation to understand the influence of ferrite-alumina oxygen carrier preparation compared with atomic layer deposition and other methods used in the literature, which included dry mixing ferrite with alumina [12]. Co-precipitation of ferrite with alumina provides even distribution and easier preparation technique with higher mixing between ferrite and alumina for hercynite cycle operation.

Experimental Methods

Sample Preparation. Co-ferrite (CF) and Co-ferrite-alumina (CFA) were prepared via constant pH co-precipitation technique utilizing respective nitrates as precursors. The materials utilized for co-precipitation were $Co(NO_3)_2.6H_2O$ (99%, Acros Organics), $Fe(NO_3)_3.9H_2O$ (ACS Reagent, $\geq$98%, Sigma Aldrich Inc.), $Al(NO_3)_3.9H_2O$ (>99%, Acros Organics), NaOH (ACS reagent, $\geq$97%, Sigma Aldrich Inc.), and Na_2CO_3 (GR ACS, anhydrous).

Mixed nitrate solutions of $Co(NO_3)_2.6H_2O$, and $Fe(NO_3)_3.9H_2O$ were prepared for Co-ferrite, and $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, and $Al(NO_3)_3.9H_2O$ for Co-ferrite-alumina. Incorporation of Co into ferrite structure increases the extent of reduction at the loss of spontaneity toward oxidation by CO_2. The literature revealed that the ratio of Co/Fe of 0.5 (which leads to $CoFe_2O_4$) provided one to obtain maximum oxygen storage capacity. Higher Co content can increase the extent of reduction while high-temperature oxidation could compensate for loss in oxidation potential via increased kinetics and thus allowing for isothermal operation. In this paper Co/Fe of 0.76 was utilized which effectively resulted in $Co_{1.3}Fe_{1.7}O_4$ (called herein as CF). For the preparation of $Co_{1.3}Fe_{1.7}O_4$, nitrate solution with appropriate Co:Fe ratio were mixed to obtain a total 1 M solution. In a continuous stirring beaker containing 0.2 M Na_2CO_3 and pH meter, the nitrate solution was added dropwise using burette along with 5 M NaOH solution to maintain a pH of 10. This resulted in the formation of precipitates, which was stirred overnight. Thus, the obtained precipitates were filtered and washed using de-ionized water until the pH was neutral followed by drying at 353 K for 24 hrs. The dried powder was then calcined at 823 K in air for 5 hrs. The calcined powder was ground to uniform size before testing.

For the preparation of CFA, appropriate nitrate solution was prepared to effectively obtain $Co_{1.3}Fe_{1.7}O_4.3Al_2O_3$. Similar procedure as given above for $Co_{1.3}Fe_{1.7}O_4$ was utilized for co-precipitation.

Fixed Bed Reactor. The prepared oxygen carriers were tested for their isothermal redox capability in a horizontal furnace equipped with alumina reactor tubing. 1 g of the ground sample was placed in the reactor tube and secured using alumina fiber wool (Zircar ceramics: Type ALBF). For reduction and oxidation steps, the total flowrate of gases was maintained at 500 sccm. Initially the reactor was heated to 1673 K in the presence of N_2 (airgas 99.998%) and maintained at this temperature for 1 h to allow for reduction step. This was followed by oxidation step for which, the flowing gases were changed to 25% CO_2 and 75% N_2 at total flowrate of

500 sccm. The evolving gases were analyzed using gas analyzer (Horiba PG-350 with NDIR) for CO_2 and CO. The oxidation step was maintained for 2 h to obtain CO. The composition of CO in the evolved gas was utilized to calculate the net CO yield, reaction rate and maximum CO flowrate. These redox cycles at 1673 K were repeated multiple times to obtain cycle stability. After three cycles, the samples were analyzed using FEI Quanta 200 scanning electron microscope (SEM) operated at 30 kV of accelerating voltage and scanning secondary electrons for its morphology in comparison with the initial sample to understand the influence of high-temperature redox operating conditions on the oxygen carrier's surface and its possible relation with cycle performance.

Results and Discussion

CO evolution was the main parameter for comparative purposes for these studies and the CO obtained from isothermal operation of CF and CFA were compared with the performance from the literature to reveal the relevance of the present study and its importance providing better performance in isothermal mode using two different types of materials.

CO Production From Co-Ferrite. Figure 1 shows the evolution of CO flowrate during isothermal redox looping at 1673 K. One of the apparent features of CO evolution from CF is the continuous evolution of CO for long time periods (relatively long for complete conversion) compared with CeO_2-based oxygen carriers. The maximum CO yield rate from CF was ~14 μmol/g·min, but it increased to 20 μmol/g·min in the second cycle followed by a decrease to 10 μmol/g·min. This variation in the maximum flowrate corresponds to the availability of surface area for reaction with CO_2. Increase from cycle #1 to cycle #2 was possibly due to incomplete calcining which led to lower flowrate in cycle #1. Then, the drop of maximum flowrate from cycle #2 to cycle #3 could be due to sintering of the oxygen carrier sample which lowered its surface area and thus lowering the surface reactions. But, as the surface reactions completed in ~30–40 min, the CO flowrate reached a plateau behavior, which suggests the reaction being limited by diffusion of gas reactants/products through CF's lattice for oxidation reaction.

Under similar conditions, maximum CO flowrate from CeO_2 reached almost 60 μmol/g·min. But in CeO_2-based isothermal redox looping, the CO flowrate dropped to 0 in 4 min that provided an average of 48 μmol/g · min over the first 90 s [24]. Although the maximum CO flowrate in the current case was lower, due to its continued reaction and isothermal nature of the reaction, longer cycle times can provide with significantly higher CO yields compared with CeO_2. Operating at higher cycle duration in isothermal conditions alleviates the concerns of this lower kinetics and allowed for higher CO yields without any significant losses. Similarly, in the case of H_2O splitting using Co-hercynite cycles at 1623 K provided maximum H_2 flowrate of 30 μmol/g · min which rapidly dropped to
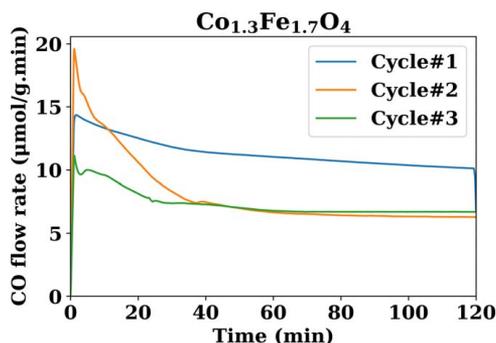

Fig. 1 Evolution of CO flowrate from oxidation step from isothermal redox looping of Co-ferrite (CF) at 1673 K for different cycles
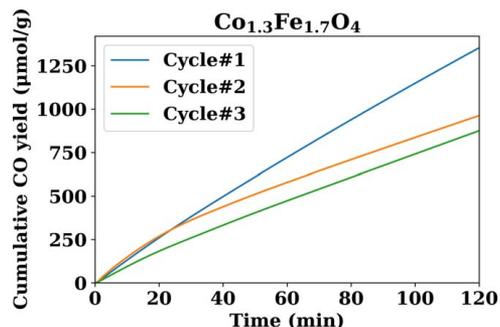

Fig. 2 Evolution of cumulative CO yield from oxidation step from isothermal redox looping of Co-ferrite (CF) at 1673 K for different cycles

6 μmol/g · min in 5–7 min and to 0 in a total of 15 min [23]. Although this provided faster cycles, under isothermal conditions, cycle duration does not affect efficiency of the process and with adjusted reactor design, it does not affect throughput. So, CF can provide constant CO flowrate allowing for easier CO capture.

Figure 2 shows cumulative CO yield with time from isothermal redox looping of CF. Cycle #1 provided with CO yield as high as 1250 μmol/g over a span of 120 min. With consecutive cycles the yield dropped to ~750 μmol/g due to sintering. Under similar conditions but for H_2O splitting, Co-hercynite in the literature yielded 102 μmol/g. Although this was obtained over relatively short cycle time, it has an overall storage capacity of the hercynite in the literature while in the current case of CF, increase in cycle duration can increase the CO yield.

Comparing with temperature swinging looping of oxygen carriers in the literature, the results shown in Fig. 2 on CO yield are significantly higher. Swinging between 1673 and 1323 K, non-stoichiometric Mn doped and other perovskites yielded only 200–250 μmol/g over 1 hr [21,25]. Some YSM perovskites reached CO yield as high as 750 μmol/g but needed temperature swing of 500 K from 1673 K as the reduction temperature which makes practicality of such reactors to decrease due to low efficiency. Different kinds of CeO_2 derived oxygen carriers also yielded less than 250 μmol/g. Only some materials such as $Co_{0.8}Zr_{0.1}Fe_2O_4/SiO_2$ provided higher yields of around 800 μmol/g over 30 min but carried out by swinging between 1673 and 1373 K [15]. Hercynites are the only ones that provide comparable results to the current case, but they were looped via temperature swinging. This suggests that although the current material may not be the best performing, it brings the significance of isothermal testing to focus as literature lacks such information. From Fig. 3, one can also observe that CF is prone to sintering. Figure 3(a) shows fresh sample morphology to contain a distribution of various particle sizes which includes particles smaller than 10 μm. But when this sample was subjected to three high-temperature CO_2 splitting cycles, the morphology changed to larger particles with significantly lowered porosity, see Fig. 3(b). This also shows that although CF provided high CO yields, due to its sintering potential, improvement of this material is still necessary for sustainable CO_2 splitting for longer durations needed in industrial scale.

CO Production From Cobalt-Ferrite-Alumina. With the pursuit of obtaining improved oxygen carrier material properties in terms of high-temperature resilience, Co-ferrite-alumina (CFA) was prepared. The composition of CFA can be effectively written as $Co_{1.3}Fe_{1.7}O_4 \cdot 3Al_2O_3$ which is similar to the above CF except for the presence of alumina. As per literature incorporation of alumina into ferrite cycle allows for hercynite cycling, which improves the reduction performance. The lack of literature on isothermal redox looping of hercynite for CO_2 splitting also motivated these examinations to gain insight into the feasibility of isothermal mode for hercynite cycling.
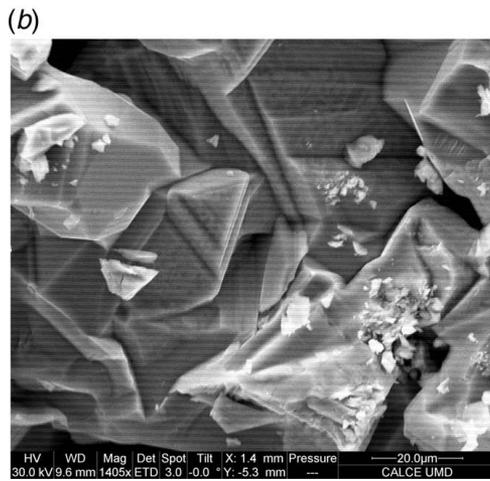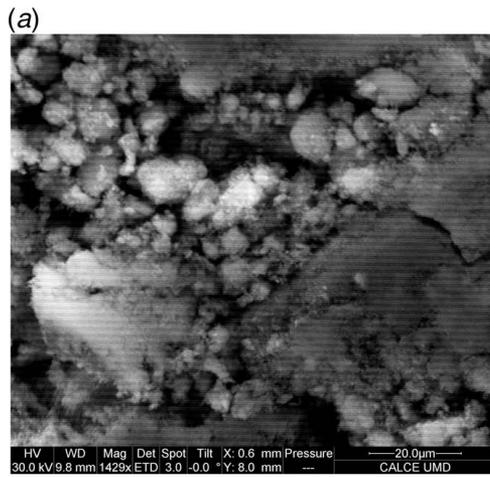
(a)

(b)

Fig. 3 SEM images of Co-ferrite, CF: (a) before and (b) after three cycles of isothermal redox looping at 1673 K with 1 hr reduction step and 2 hrs oxidation step per cycle. (a) Fresh oxygen carrier and (b) oxygen carrier after three isothermal cycles at 1673 K.

Figure 4 reveals the CO evolution from isothermal cycling of CFA. Comparison of these results with Fig. 1 directly reveals lower CO yields from CFA cycles. But it reveals that even though the flowrate is relatively lower, it is still competitive with the results in literature suggesting that this is an appropriate pathway to obtain high CO yield while gaining the advantages of isothermal operation.

Figure 5 shows cumulative CO yields, which reveal that over 2 hr cycles, CO yield of $\sim 200\,\mu$mol/g while over 1 hr, it was only
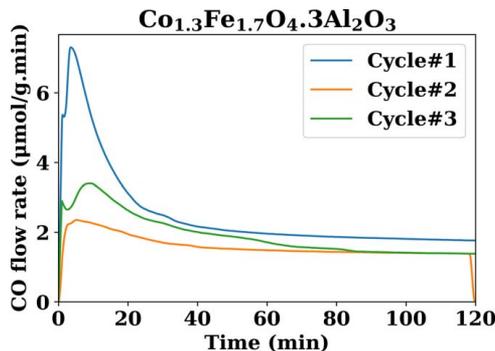

Fig. 4 Evolution of CO flowrate from oxidation step from isothermal redox looping of CFA at 1673 K for different cycles
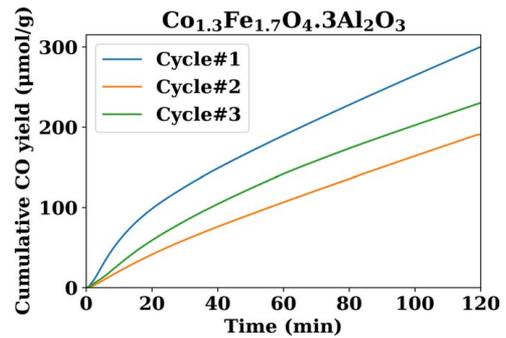

Fig. 5 Evolution of cumulative CO yield from oxidation step from isothermal redox looping of cobalt-ferrite-alumina (CFA) at 1673 K for different cycles

$\sim 100\,\mu$mol/g. These results were similar to hercynite cycle data reported in the literature, which showed almost $\sim 100\,\mu$mol/g of H_2 produced from isothermal mode [23]. Although this is not as high as the potential yield that can be obtained from hercynite cycles, it is competitive with CeO_2 and higher than temperature swinging of the same hercynite between 1673 and 1173 K [23]. This calls for further optimization of the operating conditions and
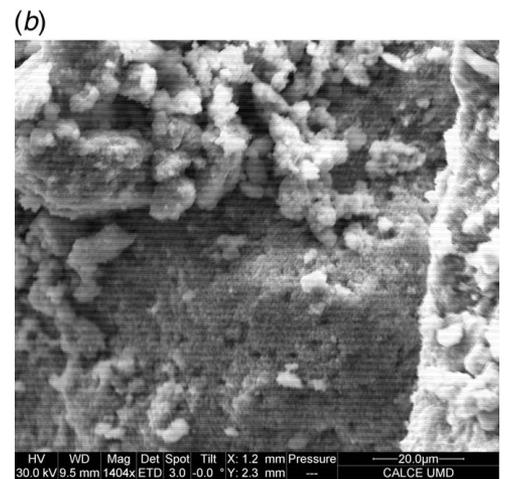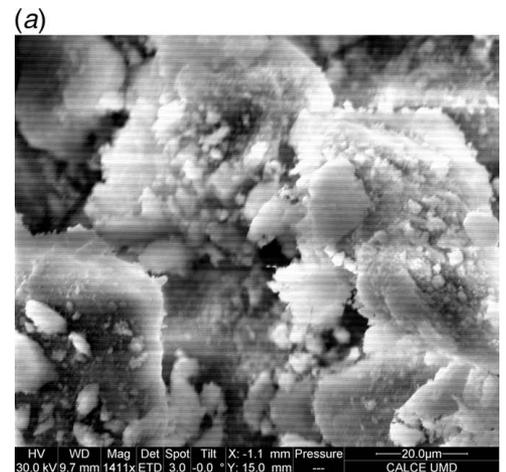

(a)

(b)

Fig. 6 SEM images of cobalt-ferrite-alumina, CFA: (a) before and (b) after three cycles of isothermal redox looping at 1673 K with 1 hr reduction step and 2 hrs oxidation step per cycle. (a) Fresh oxygen carrier and (b) oxygen carrier after three isothermal cycles at 1673 K.

the CFA composition to obtain the best possible CO yields from these materials in isothermal mode.

Figure 6 shows the promise of CFA compared with CF in terms of high-temperature resiliency and morphological stability compared with results shown in Fig. 3. Figure 6(a) showing the morphology of fresh CFA reveals similarity with Fig. 3(a) in terms of distribution of particle size, due to the utilization of co-precipitation for preparation. A comparison of Figs. 6(a) and 6(b) reveals mold increases in the number of larger size particles, but the morphology in Fig. 6(b) suffered insignificant sintering issues and maintained the structure over high-temperature operation. Compared with Fig. 3, this shows the impact of Al_2O_3 presence in providing high-temperature morphological resiliency. This also provides promise of lessened loss of CO yield over multiple cycles without the need for testing over multiple cycles. Considering this stability, development of these hercynite materials with optimized composition and isothermal temperature is necessary to obtain sustainable CO yields, while the presence of Al_2O_3 provided the morphological stability. This paper demonstrates the appreciable feasibility of ferrite class and hercynite class oxygen carriers to isothermally convert CO_2 to CO under similar gas flow conditions as temperature swinging operation. Furthermore, it provides the important advantage of isothermal operation for ease in practical application.

Conclusions

Isothermal redox looping for CO_2 splitting provides practical advantages of faster reaction, throughput, lessened losses from solid–solid heat recovery and time taken for temperature swinging along with lowered thermal fatigue in oxygen carriers and reactor materials. The literature does not reflect this importance and contains significant knowledge gap in this field. This paper demonstrates the importance of isothermal redox looping for CO_2 conversion using Co-ferrite and Co-ferrite-alumina (hercynite cycle) along with appropriate comparison from the literature with other isothermally tested oxygen carrier materials to reveal the performance of different oxygen carriers in temperature-swing redox looping. Co-ferrite provided significantly high CO yields and flow-rate compared with those reported in the literature. CO yields as high as 750 $\mu mol/g$ from only 25% CO_2 flow (125 sccm) in isothermal mode offers very promising results which are higher compared with the performance reported in the literature on temperature swinging CeO_2, perovskites and isothermal CeO_2 and hercynite. Similar testing of Co-ferrite-alumina revealed relatively lower CO yields compared with its ferrite counterpart, but the results were similar to the isothermal hercynite cycle reported in the literature on H_2O splitting. The potential for lowering of reduction temperature suggests that further optimization of isothermal operational conditions and the composition of this hercynite oxygen carrier requires further examination. Morphological studies revealed significant promise of Co-ferrite-alumina in maintaining its surface area and thus CO yield over multiple redox cycles compared with Co-ferrite which showed significant decrease in the porosity and surface area. This reveals the need for further studies into isothermal operation of hercynite cycles for enhanced CO production and the development of isothermal reactors prior to pilot-scale demonstration using renewable energy such as concentrated solar power to easily scalable CO_2 conversion and CO production.

Acknowledgment

Conflict of Interest

There are no conflicts of interest.

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