Batch fluidized bed study of the interaction between alkali impurities and braunite oxygen carrier in chemical looping combustion

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Abstract

Chemical looping combustion (CLC) is a novel technology for heat and power generation with low-penalty CO_2 capture. Using biomass in CLC (bio-CLC), negative CO_2 emission can be attained. Alkali (mainly K and Na) in biomass can be problematic in bio-CLC, as it can interact with the oxygen carrier bed. The current work used charcoal and four charcoal samples impregnated with K_2CO_3, Na_2CO_3, KCl and NaCl, respectively, to study alkali interaction with a low-alkali braunite manganese ore oxygen carrier. The experiments were successfully carried out at 950°C in a quartz batch fluidized-bed reactor. For each alkali-fuel sample, more than 30 cycles of redox were performed. Using the solid fuel impregnated with K_2CO_3, Na_2CO_3, KCl and NaCl, char gasification was improved by a factor of 10, 8, 4 and 3 as compared to the non-impregnated fuel. Partial-defluidization of the braunite particles was found with all the alkali-fuels, although the extent differed, e.g. K_2CO_3 and KCl resulted in earlier onset of partial defluidization than Na_2CO_3 and NaCl. Hard agglomeration was never observed, while soft partial agglomeration was seen. Accumulation of K, Si, and Ca in agglomerates and particle boundary was found after cycles with K_2CO_3- and KCl-charcoal, while Na, Si and Ca was found after the Na_2CO_3- and NaCl-charcoal cycles. The mechanism of agglomeration formation seems different for these alkali-charcoals. For K_2CO_3- and KCl-charcoal, it seems the potassium reacted with Fe and Mn in the braunite, forming low-melting point components and thus led to agglomeration. In the case of Na_2CO_3- and NaCl-charcoal, direct reaction with the braunite was not seen, and it seems as if other reactive species combined were formed, which acted as a binder between particles to form agglomerates. In addition, after cycles with the K_2CO_3- and Na_2CO_3- charcoals, 80% K and 40% Na were retained in the oxygen carrier particles. After the use with all the alkalis, the braunite reactivity with CH_4, CO and H_2 was similar to the fresh particles. It is clear that alkali species could react with the braunite oxygen carriers, and this could affect reactivity and fluidization tendency in the long run. Still, only soft agglomerates and partial defluidization were found, which may not be the case in a real CLC system operating at higher fluidizing velocities.

Keywords: CO_2 capture; Chemical looping combustion; bio-CLC; alkali; defluidization

1. Introduction

Chemical looping combustion (CLC) is a novel technology, which uses a transition metal oxide (called oxygen carrier) to provide atomic oxygen for fuel combustion. Fuel in CLC never mixes with air, thus resulting in a CO_2 stream undiluted by air-nitrogen. The separation of CO_2 from combustion products, $CO_2 + H_2O$, can be realized by simple condensation, thus low energy penalty is needed for CO_2 capture in CLC. Manufactured materials, naturally occurred ores (iron ore, ilmenite, manganese ore, etc.) and industrial by-products (redmud, steel slag, etc.) have been tested in CLC systems. Among these materials, natural ores are widely studied worldwide due to their low cost and being environmentally benign. Use of biomass makes CLC (bio-CLC) more attractive in view of the rapidly diminishing carbon budget for the target of maximum 1.5°C temperature rise, because CO_2 will be captured from the atmosphere through a bio-CLC process and negative CO_2 emissions will be attained. Demonstration of bio-CLC has been successfully performed in 0.5-100 kW_{th} pilot units for CLC [1-3] and even partial CLC in a 12 MW_{th} boiler [4], and more research is needed.

Ash from solid fuels is incombustible in CLC and it is the main residue after the devolatilization of fuel and gasification of char. When using biomass in bio-CLC process, the effect of fuel ash requires attention, as alkalis (K and Na) in biomass, especially herbaceous biomass, is present in much higher proportion as compared to coal ash. In a gasification process, these alkalis can catalyze the char gasification and thus result in faster biomass conversion [5]. Nevertheless, the high alkali concentration in biomass is also a main reason for bed agglomeration. In addition, derivates from alkalis (e.g. alkali chlorine) contribute to fouling heat exchanger surfaces and reactor walls. Effect of alkali will be different in CLC process as compared to conventional combustion. Because the heat transfer surfaces are placed in the air reactor where exothermic reactions happen, whereas no heat exchangers are placed in the fuel reactor although alkalis are mainly released there [6]. This reduces the contact of alkalis with the heat transfer surfaces, thus lowers the risk of operation failures from corrosion and/or fouling in CLC. Nonetheless, oxygen carrier is in direct contact with ash in the fuel reactor, and this may lead to oxygen carrier and ash interactions [7] that could be both advantageous and disadvantageous for CLC operation. Impregnation of K^+ or Na^+ in an ilmenite oxygen carrier has greatly promoted the reduction activity of the ilmenite with CO [8]. But it seems the reactivity depends a lot on the type of alkali and oxygen carrier [9]. Apart from the reactivity, the fluidization and agglomeration behaviour are other important issues in the presence of alkali. Alkali species with low-melting point are usually considered responsible for gluing/sticking oxygen carrier particles together, causing agglomerations. In operation of a 60 kW_{th} and a 100 kW_{th} CLC pilot units, the gas-phase alkalis have been measured and evaluated and alkali retention in the oxygen carrier material was significant [10, 11]. The retention may further lead to impact on oxygen carrier reactivity and incur interactions of alkali elements with the bed. This could cause unstable operation and even defluidization/agglomeration, as a result of formation of alkali-based compounds which usually have low-melting point. Thus, the effect of alkalis is important to explore for the bio-CLC process, and more research is needed.

This work studies the interaction of K and Na alkalis with a braunite manganese ore in a batch fluidized bed reactor at 950°C. Alkali salts (K_2CO_3, Na_2CO_3, KCl and NaCl) were impregnated in charcoal particles and injected into the reactor, providing reducing environment of the reduction step in redox cycles. Part of the results for K_2CO_3- and Na_2CO_3- charcoal were from our previous work which at this moment is submitted for publication [7]. More than 30 cycles were conducted to explore the defluidization/agglomeration behaviour induced by the interaction between the alkalis and oxygen carrier. Reactivity of the bed material was regularly checked after middle and final cycles with the alkali-charcoal samples. The composition and microstructure of the fresh oxygen carrier, and samples from the middle and final cycles were analyzed by various techniques.

2. Experimental

2.1. Fuel and braunite oxygen carrier

Methane, syngas (50%CO+50%H_2), charcoal and charcoal samples impregnated separately with K_2CO_3, Na_2CO_3, KCl and NaCl salts were the fuels used. The charcoal contains 84.3% fixed carbon, 4.9% volatiles, 8.9% ash and 1.9% moisture. The four alkaline salts mentioned above were separately impregnated in charcoal samples and used in the fluidized bed experiments to study their interactions with the oxygen carrier. The amounts of alkalis impregnation are theoretically equivalent to 13.12% Na_2CO_3, 18.65% K_2CO_3, 23.84% NaCl and 29.58% KCl of final fuel weight. The oxygen carrier studied in the current work is called braunite which is a manganese ore investigated in previous pilot operations [10]. Main metal elements in the non-impregnated charcoal and braunite are presented in Table 1, and the alkalis (K and Na) are very low in both samples.

Table 1. Main metal components in the Charcoal and braunite

	Mn	Fe	Si	Ca	K	Na
Charcoal	<0.01	0.27	2.7	0.11	0.05	0.03

Braunite	52.0	11.0	2.6	2.5	0.22	0.29

2.1. Reactor setup and test procedure

A fluidized bed reactor was used to study the oxygen carrier reactivity with gaseous fuels, interaction with alkalis and bed fluidization. As shown in Figure 1, the reacting/fluidizing gas stream is switched and controlled by three automatic valves on the right-side. These valves switch the reaction environment among reduction, inert and oxidation. The gas stream enters the quartz reactor from the bottom and the reactor was heated by a surrounding electric oven. In reduction, gaseous fuels (CH_4 and syngas) enter the reactor from the bottom inlet while the solid fuels were led into the reactor from the top and accompanied with a continuous sweeping N_2. A pressure transducer connecting the reactor inlet and outlet was used to monitor the pressure drop over the bed to reflect the fluidization status. Downstream of the reactor is an electric cooler and a gas analyzer. The cooler removes steam from the outlet gas stream before the gas was sent to the analyzer. Concentrations of CH_4, CO, CO_2, H_2 and O_2 and the pressure signal were sampled. All data were registered in a computer connected to a data logger.

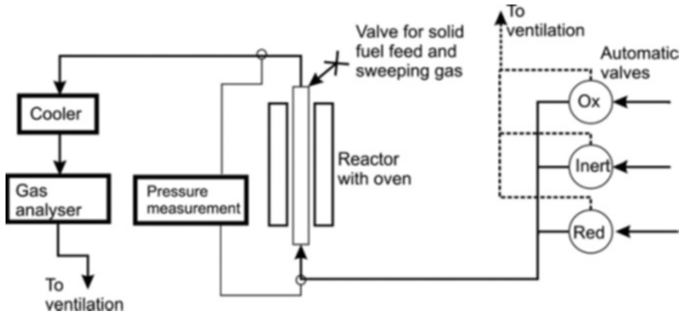

Figure 1. Schematic description of the fluidized bed reactor system

For all the tests, the reaction temperature was set to 950°C. In the gaseous fuel tests, the inlet flow rate was kept at 345 ml/min for CH_4 and 450 ml/min for the syngas, corresponding to $u_g/u_{mf}=9$ and 12, respectively. The bed was 20 g braunite in the case with CH_4 and a mixture of 2 g braunite and 15 g sand in syngas reactions. The latter conditions were employed as to not fully convert the fuel, facilitating the data evaluation. In the solid fuel experiments, around 0.1 g solid fuel particles are injected from the reactor top with a 300 ml/min sweeping N_2. Gasification/fluidization gas is a mixture of 48% H_2O and 52% N_2 with a total flow rate of 865 ml/min corresponding to $u_g=0.4$ m/s and $u_g/u_{mf}=31$. Apart from syngas tests, the experimental procedure with K_2CO_3-charcoal and Na_2CO_3-charcoal and CH_4 is shown in Figure 2. Similar routine is repeated for KCl- and NaCl- charcoals, which are not presented in Figure 2. In general, the oxygen carrier was first activated and/or stabilized during cycles with CH_4 and then used with solid fuel experiments. Afterwards, the charcoal was used for 2-3 cycles to be considered as reference without alkali presence. Then, the oxygen carrier is exposed to numerous cycles with K_2CO_3-charcoal, Na_2CO_3-charcoal, KCl-charcoal or NaCl-charcoal. The alternating use of normal charcoal and alkali-fuel is repeated for several rounds. The entire campaign was finalized with a total cycle number of 30-53 depending on alkali types. Samples from the middle cycles called “K_2CO_3-middle”, “Na_2CO_3-middle”, “KCl-middle” or “NaCl-middle” were taken for characterizations. And the sample in the end of campaign is denoted as “K_2CO_3-final”, “Na_2CO_3-final”, “KCl-final” or “NaCl-final”. Reactivity of these middle and final oxygen carrier samples was evaluated by the reactions with CH_4. And extra experiments were performed for syngas with the fresh and used braunite samples and not shown in Figure 2. Based on these gaseous experiments, the reactivity variation was evaluated and compared.

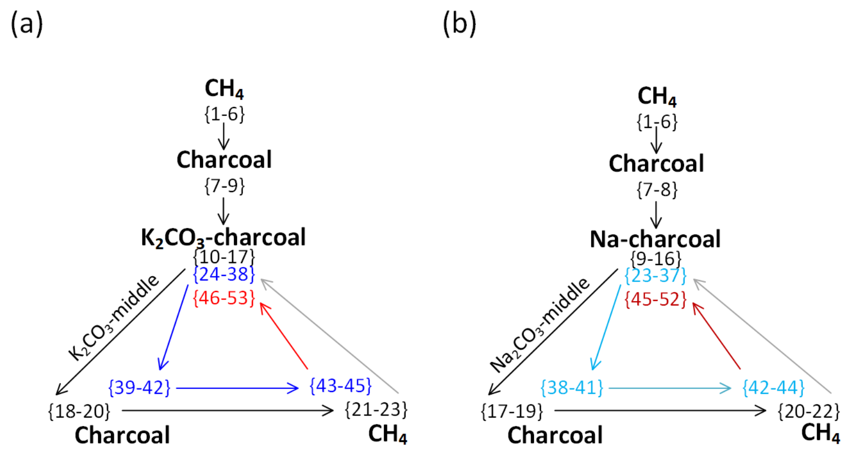

Figure 2. The two series of experiments with e.g. (a) K_2CO_3-charcoal and (b) Na_2CO_3-charcoal. The consecutive cycle numbers are presented in brackets. Arrows show the experimental flow stream.

3. Data evaluation

Mass-based conversion, ω, of the oxygen carrier was calculated based on oxygen balance, gas concentrations and exit gas flow during the reactions with CH_4 and syngas. The total dry gas flow, $\dot{n}_{out}$, leaving the reactor was calculated based on calibration or carbon balance. M_O is the molar mass of atomic oxygen and m_{ox} the mass of oxygen carrier in the bed. x_{CO2}, x_{CO} and x_{H2} are the measured concentrations at time t.

$$\omega_{CH_4} = 1 - \int_{t_0}^{t} \frac{\dot{n}_{out} M_O}{m_{ox}} \left(4x_{CO_2} + 3x_{CO} - x_{H_2}\right) dt \quad (1)$$

$$\omega_{syn} = 1 - \int_{t_0}^{t} \frac{\dot{n}_{out} M_O}{m_{ox}} \left(2x_{CO_2} + x_{CO} - x_{H_2}\right) dt \quad (2)$$

Gas yield, γ_i, of CH_4 and CO or H_2 in syngas represent the extent of fuel conversion in the reduction. This parameter reflects the efficiency of oxygen transfer from the oxygen carrier to the fuel gases and was calculated from instantaneous gas concentrations.

$$\gamma_{CH_4,CH_4} = \frac{x_{CO_2}}{x_{CH_4} + x_{CO} + x_{CO_2}} \quad (3)$$

$$\gamma_{CO,syn} = \frac{x_{CO_2}}{x_{CO} + x_{CO_2}} \quad (4)$$

$$\gamma_{H_2,syn} = 1 - \frac{x_{H_2}}{x_{CO} + x_{CO_2}} \quad (5)$$

The braunite reactivity with CH_4, CO and H_2 can be represented with the rate constant k_i, calculated via Eqs. (6)-(8) below, under the assumptions of atmospheric operation pressure and first-order reaction between the fuel components and oxygen carrier. V_{CH4} and V_{syn} are the volumetric flow of methane and syngas entering the reactor, ε is the volumetric expansion ratio for full CH_4 combustion.

$$k_{F,CH_4} = \frac{V_{CH_4}\left(-(1+\varepsilon)\ln(1-\gamma_{CH_4}) - \varepsilon\gamma_{CH_4,CH_4}\right)}{m_{ox}} \quad (6)$$

$$k_{F,CO} = \frac{V_{syn}\left(-\ln(1-\gamma_{CO,syn})\right)}{m_{ox}} \quad (7)$$

$$k_{F,H_2} = \frac{V_{syn}\left(-\ln(1-\gamma_{H_2,syn})\right)}{m_{ox}} \quad (8)$$

The total mass of carbon at time t, $m_C(t)$, leaving the reactor can be calculated using the concentrations of carbonaceous gases and total outlet gas flow rate in reduction. M_C is the molar mass of atomic carbon.

$$m_C(t) = \int_{t_0}^{t} \dot{n}_{out} M_C \left(x_{CH_4} + x_{CO_2} + x_{CO}\right) dt \quad (9)$$

Thus, the carbon conversion from the solid fuels as a function of reaction time, $X_C(t)$, can be easily obtained as the ratio between $m_C(t)$ and the total amount of carbon from the reactor exit, $m_{C,tot}$.

$$X_C(t) = \frac{m_C(t)}{m_{C,tot}} \quad (10)$$

The rate of char gasification, r_{inst}, is based on residual amount of carbon in the reactor using the above obtained carbon conversion data.

$$r_{\mathrm{inst}} = \frac{1}{1-X_{\mathrm{C}}}\frac{dX_{\mathrm{C}}}{dt} \tag{11}$$

Fluidization state of the bed was evaluated by the amplitude of pressure drop fluctuation, σ, based on the data from middle period of the oxidation step. This middle period was selected from a data segment without influence from steam addition and gas switching.

$$\sigma = \left(\frac{1}{N-1}\cdot\sum_{n=1}^{N}\left(\Delta p_n - \Delta p_{avg}\right)^2\right)^{0.5} \tag{12}$$

where N is the total number of pressure-drop values that were used for calculation, Δp_n the nth pressure drop value used and Δp_{avg} is the average of the N pressure-drop values.

4. Results and discussion

4.1. Reaction with CH_4 and syngas

Figure 3 shows a typical cycle composed of reduction with CH_4 or syngas (“CH_4” or “Syn”), inert (“N_2”) and oxidation (“4.5% O_2”). More than 70% of CH_4 was not converted and the peak concentrations of CO_2 and CO are only 11.5% and 1.1%, respectively, indicating a low reactivity of the braunite with CH_4. Although significant proportions of CH_4 were not converted, carbon deposition was not seen, as no carbonaceous gas was detected in the following oxidation. The reaction with syngas has a better reactivity, as higher conversions of CO and H_2 in the syngas were reached, i.e. the residual CO is at around 30%, while the H_2 is less than 7%.

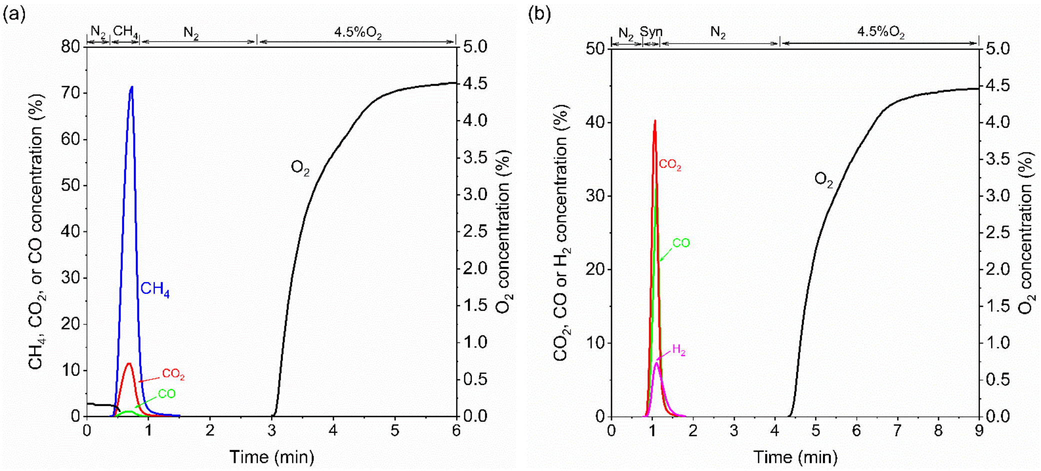

Figure 3. Concentrations of CH_4, CO, CO_2, H_2 and O_2 as a function of time for a typical cycle between braunite and (a) CH_4 and (b) syngas at 950°C.

4.2. Reaction with solid fuels

Using charcoal and alkali-charcoals, typical reduction periods are shown in Figure 4. In the case of non-alkali impregnated fuel, the addition of solid fuel initially led to a short and small peak of CH_4 from the residual volatiles, while CO and H_2 from steam gasification are seen to gradually decrease. The main gas detected, however, is CO_2. Thus, most of the CO and H_2 intermediates reacted with the braunite to CO_2 and H_2O. The unconverted H_2 has a higher concentration than CO although the former usually has a higher reactivity than the latter. This can be explained by water-gas shift reaction, which converts part of CO and H_2O to CO_2 and H_2 in steam rich conditions. Complete conversion of charcoal takes around 15 min and has a long tail of CO_2, H_2 and CO concentration. As the fuel was changed to KCl-charcoal and K_2CO_3-charcoal, the char gasification is faster, i.e. around 10 min and 5 min are sufficient for complete conversion. This is a result of catalytic effects of the K and Na. Promotion on gasification rate as compared to charcoal was also noticed with NaCl-charcoal and Na_2CO_3-charcoal.

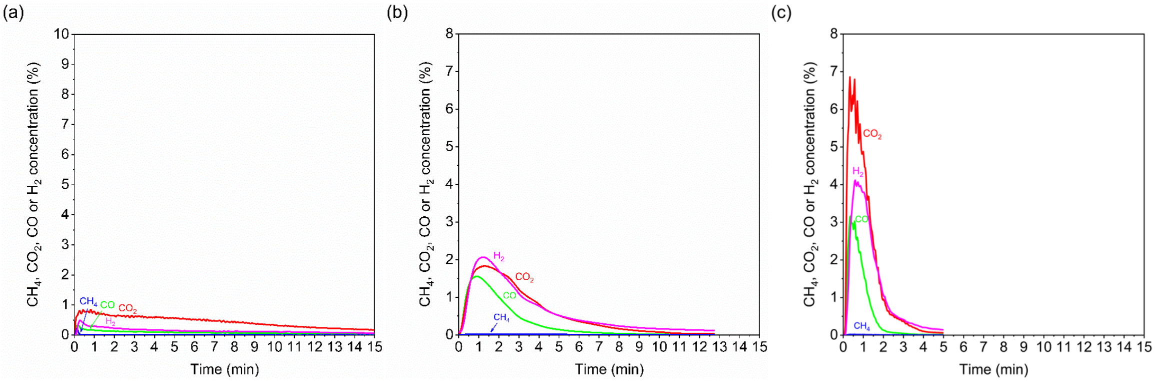

Figure 4. Concentrations of CH_4, CO, CO_2 and H_2 during the braunite reduction with (a) charcoal, (b) KCl-charcoal and (c) K_2CO_3-charcoal at 950°C under the fluidization with 48% H_2O+52% N_2.

4.3. Rate of gasification

The rate of char gasification is plotted against carbon conversion for charcoal, KCl-charcoal, NaCl-charcoal, K_2CO_3-charcoal and Na_2CO_3-charcoal in Figure 5. As expected, the charcoal impregnated with alkalis has a higher gasification rate. KCl-charcoal has a rate of around 2.5 times that of charcoal and NaCl-charcoal is about 4 times that of charcoal. In the case of K_2CO_3-charcoal and Na_2CO_3-charcoal, the gasification rate are 10-12 times higher as compared to charcoal. Obviously, K_2CO_3 and Na_2CO_3 can promote the gasification much better than KCl and NaCl.

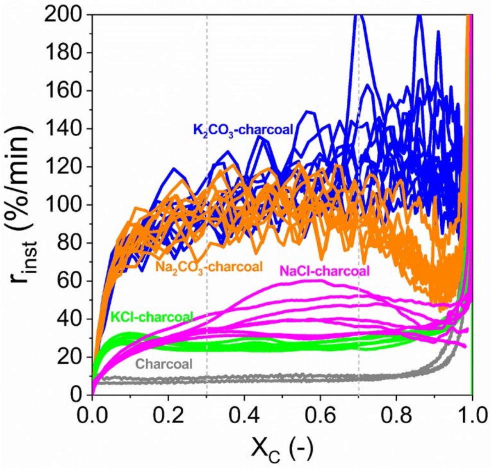

Figure 5. Rate of char gasification as a function of carbon conversion for charcoal, KCl-charcoal, NaCl-charcoal, K_2CO_3-charcoal and Na_2CO_3-charcoal. Different curves in a same colour show the cycle number with a specific fuel.

4.4. Partial defluidization

An example of bed fluctuation amplitude σ is given in Figure 6 for K_2CO_3-charcoal and Na_2CO_3-charcoal series of experiment. In cycle 1-6 with CH_4, the fluctuation amplitude was at 0.035-0.045 for K_2CO_3-charcoal and Na_2CO_3-charcoal series, and this indicates good fluidizations. The amplitude of fluctuation was not greatly changed in the cycles with charcoal, i.e. cycle 7-9 for K_2CO_3-charcoal series and cycle 7-8 for Na_2CO_3-charcoal series. However, afterwards, an abrupt drop of fluctuation amplitude was observed for K_2CO_3-charcoal. After cycle 10 which was the first cycle with K_2CO_3-charcoal the amplitude was usually less than 0.03. In the case of Na_2CO_3-charcoal, the fluctuation amplitude was 0.03-0.04 in cycle 9-16 using Na_2CO_3-charcoal. However, this was decreased to less than 0.025 after cycle 17. The low pressure-fluctuation amplitudes coincide with the observed several agglomerates of bed particles after the reactor cooling down. After cycle 10 for K_2CO_3-charcoal series and cycle 17 for Na_2CO_3-charcoal series, the fluctuation amplitude was relatively stable at 0.005-0.01. In addition, K_2CO_3-charcoal can lead to partial defluidization and partial agglomeration faster than Na_2CO_3-charcoal, i.e. start from cycle 10 versus from cycle 17. The amplitude of pressure drop in the cases with KCl-charcoal and NaCl-charcoal is under analysis. And the first impression is similar to K_2CO_3-charcoal and Na_2CO_3-charcoal. However, is seems the partial defluidization and partial agglomeration showed little effect on the braunite's reactivity as discussed below in Section 4.7.

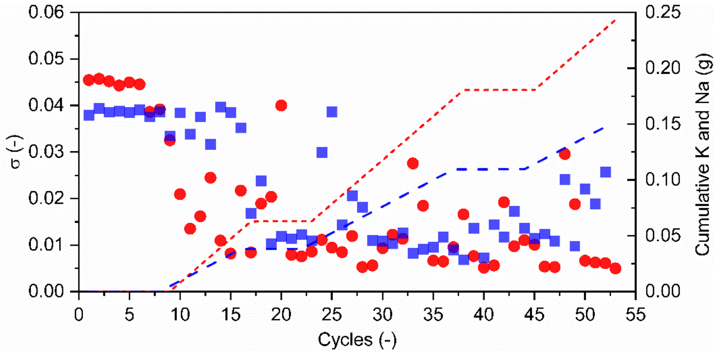

Figure 6. Amplitude of pressure drop fluctuations (K_2CO_3-charcoal: ● and Na_2CO_3-charcoal: ■) and the calculated cumulative amount of K_2CO_3 (- -) and Na_2CO_3 (——) in the braunite as a function of cycle number.

4.5. Agglomerates and alkali distribution

Partial agglomeration of the braunite bed was found after cycles with K_2CO_3-charcoal, Na_2CO_3-charcoal, KCl-charcoal or NaCl-charcoal. As shown in Figure 7, the agglomeration is clearly seen as bridges between particles. Line scanning from SEM-EDX characterization suggests the main elements in the bridges are Si, Na and Ca for the braunite used with the Na_2CO_3- and NaCl impregnated fuels. On the other hand, the main particles mainly contain Mn and Fe, while these are extremely low in the bridges. This phenomenon indicates Mn and Fe may not take part in the agglomerate's formation. However, in the case of the used oxygen carrier with K_2CO_3-charcoal and KCl-charcoal, Si, K, Ca, Mn and Fe are rich in the agglomerate bridges. Thus, it seems Mn and Fe took some roles in the agglomeration during cycles with charcoal impregnated with K_2CO_3 and KCl. Presumably, potassium in the case of K_2CO_3-charcoal and KCl-charcoal can interact with Mn and Fe, resulting in low-melting point compounds, which melted and stuck particles together to form agglomerates.

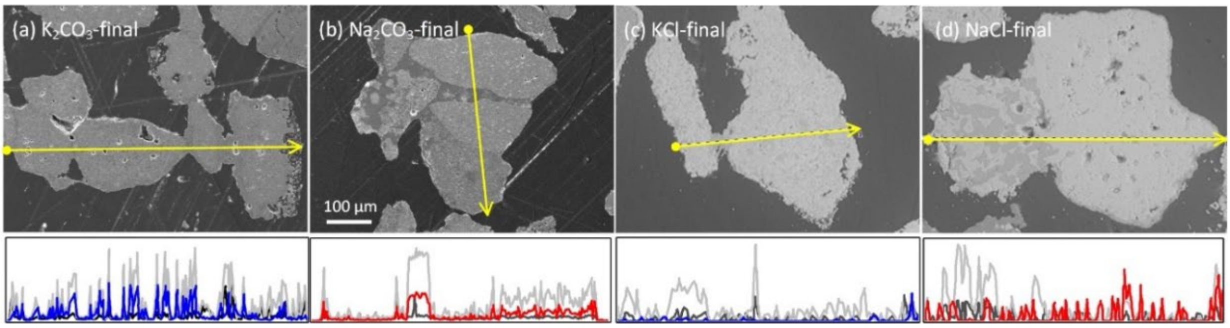

Figure 7. SEM-EDX analyses of agglomerates from the bed material after final cycles with alkali-charcoal samples: (a) used with K_2CO_3-charcoal, (b) used with Na_2CO_3-charcoal, (c) used with KCl-charcoal and (d) used with NaCl-charcoal. Yellow arrow shows the scanning line and the panels below the element (Ca: —, Si: —, K: —, Na: —) distribution along the scanned line.

4.6. Alkali retention in the braunite particles

In Figure 8, the amount of K and Na measured in the K_2CO_3-middle, Na_2CO_3-middle, K_2CO_3-final and Na_2CO_3-final braunite samples is compared to the theoretical cumulative alkali addition with fuel (K_2CO_3- and Na_2CO_3-charcoal). Both data were calculated based on the ICP-OES analyses of the samples. Most of the Na introduced with Na_2CO_3 is retained in the braunite, whereas less than half of the K is retained, showing a lower affinity of K with the braunite bed. This indicates a higher tendency of Na interaction with the braunite than K in the case of using Na_2CO_3-charcoal and K_2CO_3-charcoal. Total added K and Na with K_2CO_3-charcoal and Na_2CO_3-charcoal was 0.16 and 0.24 g which is 0.8-1.2% of the braunite weight. In the final samples, around 40% of K and 80% of Na added have retained in the braunite oxygen carrier. The retention of K and Na could be a result of agglomeration, meaning the alkalis can stay in the agglomerates mainly on the particle surface, as seen in the SEM-EDX results. The retention of K and Na in the case of KCl- and NaCl-charcoal experiments seems less than K_2CO_3-charcoal and Na_2CO_3-charcoal experiments, and the final analyses are ongoing.

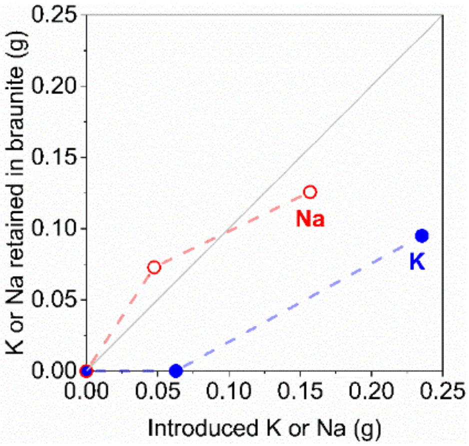

Figure 8. Retention of K and Na in the braunite as a function of cumulative amount of K and Na introduced with the solid fuels (K_2CO_3-charcoal and Na_2CO_3-charcoal).

4.7. Evolution of braunite reactivity

The fresh and used oxygen carrier samples were tested with CH_4 and syngas to evaluate the reactivity with CH_4, CO and H_2. The rate constant as a function of the mass-based oxygen carrier conversion is shown in Figure 9. In general, the rate constant decreases gradually as the oxygen carrier is more reduced, i.e. a lower rate constant at a lower value of conversion. The braunite used with K_2CO_3-charcoal, Na_2CO_3-charcoal, KCl-charcoal or NaCl-charcoal has the rate constant varying in the range of 0.03-0.1 $L_n/(kg\cdot s)$ and the conversion changing between 1 and 0.997. In the case of CO and H_2, the rate constant for samples used with K_2CO_3-charcoal or Na_2CO_3-charcoal is much higher than CH_4 and has a wider range of oxygen carrier conversion, i.e. from 1 to 0.965. Further, the rate constant for H_2 is in the range of 4.5-8.7 $L_n/(kg\cdot s)$, which is higher than that for CO, i.e. 1.5-5.1 $L_n/(kg\cdot s)$. Figure 9(b) shows the rate constant in a typical reduction with CH_4 for the braunite after the KCl-charcoal and NaCl-charcoal use, and similar conclusion as K_2CO_3 and Na_2CO_3 cases can be obtained. The rate constant for CO and H_2 with braunite after use with KCl-charcoal and NaCl-charcoal is under analyses. Based on the present results, the reactivity of fresh, K-final and Na-final braunite samples are similar, although the materials have accumulated K or Na and undergone partial defluidization and partial agglomeration.

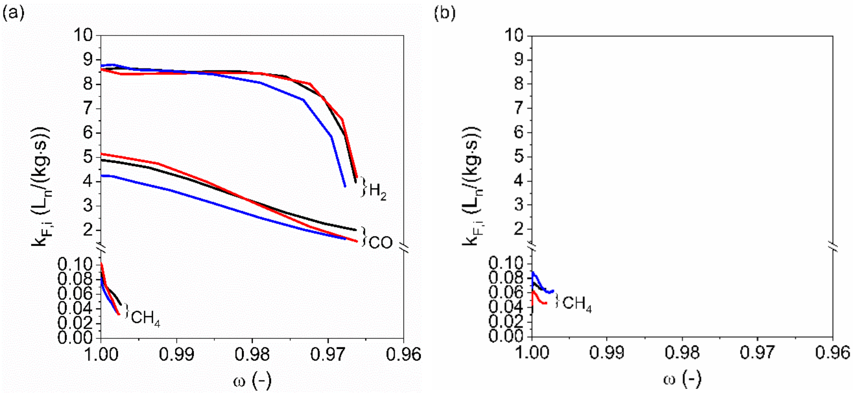

Figure 9. Rate constant for CH_4, CO and H_2 versus mass-based oxygen carrier conversion for fresh (—, black lines), K-final (—, blue lines) and Na-final (—, red lines) braunite samples: (a) after use with K_2CO_3-charoal or Na_2CO_3-charcoal and (b) after use with KCl-charoal or NaCl-charcoal.

Conclusions

The presence of K or Na in the solid fuel resulted in a char gasification rate of 3-10 times that of charcoal, demonstrating alkali catalytic effects. Partial agglomerations and partial defluidization of the braunite bed were detected in the cycles with K_2CO_3-charcoal, Na_2CO_3-charcoal, KCl-charcoal or NaCl-charcoal. Earlier partial agglomeration/defluidization was found with K_2CO_3-charcoal and KCl-charcoal. K, Na, Si and Ca were enriched on the particle surfaces as well as in the bridges among agglomerated particles. No Fe or Mn was found in the agglomerates of the braunite particles used with Na_2CO_3-charcoal or NaCl-charcoal, while this is not the case for K_2CO_3-charcoal and KCl-charcoal.

Thus, different mechanisms are expected for agglomerations in K-charcoal and Na-charcoal cases. Presumably, oxygen-carrier surface melting for K-charcoal and oxygen-carrier particles gluing from possible new-formed components for Na-charcoal are the mechanisms of agglomerating. Braunite retention of K and Na from fuel added was founded, with K having up to 40% retention and Na up to 80%. Despite partial agglomeration and alkali retention, the reactivity of braunite with CH_4, CO and H_2 was essentially the same as that of the fresh oxygen carrier.

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