

## Gasification of bamboo carbon with molten alkali carbonates

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**Abstract**—Solid carbon can be used as a fuel in the direct carbon fuel cell (DCFC). The chemical oxidation of carbon with alkali carbonates was investigated in this work. Decreasing the weight ratio of carbon to carbonate from 5 g : 5 g to 5 g : 20 g had an insignificant effect on the amount and concentration of gases. However, changing the amounts from 5 g : 5 g to 20 g : 20 g tripled the total amount of gases produced with similar gas compositions. The gas compositions ranged from 62.2-67.5 mol% CO, 13.9-14.7 mol% H<sub>2</sub>, and 5.7-16.8 mol% CO<sub>2</sub> at 800 °C. Thus CO was the dominant gas species in the conditions. With increasing temperature, CO generation was activated, especially over 700 °C. The carbonate species did not affect carbon oxidation. Steam was supplied to the carbon and carbonate mixture at a fixed flow rate of N<sub>2</sub> or air. H<sub>2</sub> was the highest composition at both cases.

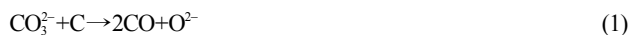
Key words: Gasification, Bamboo Carbon, Molten Carbonates, Nitrogen, Steam

### INTRODUCTION

Recently, solid carbon has been used as a fuel for the direct carbon fuel cell (DCFC). In general, most fuel cells use hydrogen, as it is the most reactive gas, and thus a hydrogen-supplying unit is required for the fuel cell. However, the complexity of hydrogen units negatively affects the economics of fuel cells and their applications. Carbon, however, is a solid phase that has much higher energy density than gas fuel, and it can be obtained from all organic materials. Thus the source of carbon is in principle inexhaustible.

The DCFC was developed based on the molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC), and molten hydroxide technology [1,2]. Unlike hydroxide technology, DCFC with MCFC and SOFC technologies employs molten alkali carbonates as the catalyst for the solid carbon [3,4]. In previous studies, the alkali carbonates were reported to enhance the rate of carbon oxidation [5] and DCFC performance [3].

Nagase et al. [6] reported that different oxidation mechanisms act in the combination of carbon with Li<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>. Carbon with Li<sub>2</sub>CO<sub>3</sub> is oxidized by the following intermolecular redox reaction:



On the other hand, they suggested that carbon with Na<sub>2</sub>CO<sub>3</sub> oxidizes to CO through a disproportionation reaction of the gas phase metal and metal peroxide path, with a comparable rate to the reverse Boudouard reaction (Eq. (2)).



They also reported that the rate of conversion of C to CO with Na<sub>2</sub>CO<sub>3</sub> is about 23 times faster than that with Li<sub>2</sub>CO<sub>3</sub>.

In general, the characteristics of alkali carbonates of Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub> are determined by the alkali metal ions. Li<sub>2</sub>CO<sub>3</sub>,

with the smallest Li ion, has the highest ionic conductivity among such ions, while the large ionic size of K allows high gas solubility [7]. Subsequently, the eutectic of Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> (Li-Na) showed higher ionic conductivity than Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> (Li-K) whereas the Li-K carbonates showed greater gas solubility than Li-Na melt [7].

The alkali carbonates also catalyze carbon steam reforming (csr) (Eq. (3)) [5].



Carbon steam reforming changes carbon to H<sub>2</sub> and CO. Thus csr is a way of using carbon to supply H<sub>2</sub> and CO as fuel for the MCFC and SOFC.

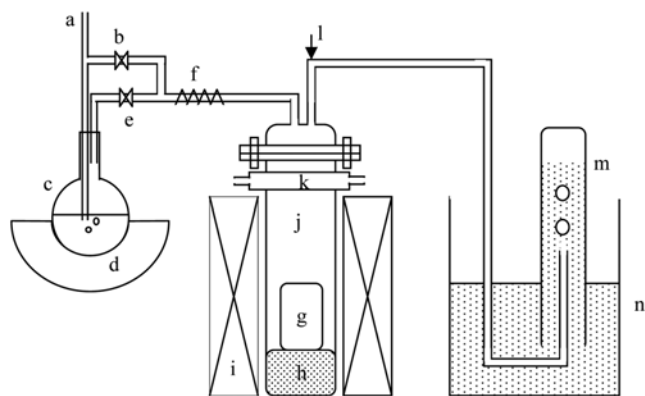
In this work, activated carbon made from bamboo was oxidized with Li-K, Li-Na, and Li-Na-K eutectic carbonates under N<sub>2</sub> and H<sub>2</sub>O environments. The resulting gas compositions were analyzed via gas chromatography. The concentrations and amounts of gases produced revealed the chemical oxidation behavior of the carbon.

### EXPERIMENTAL SECTION

The carbon made from bamboo was a commercially available activated carbon supplied by Shinkwang Chemicals (Korea). Its average particle size was about 0.5 mm, and it was used as received. Carbonates of the following compositions were employed: 62 mol% Li<sub>2</sub>CO<sub>3</sub>+38 mol% K<sub>2</sub>CO<sub>3</sub> (Li-K), 53 mol% Li<sub>2</sub>CO<sub>3</sub>+47 mol% Na<sub>2</sub>CO<sub>3</sub> (Li-Na), 43.5 mol% Li<sub>2</sub>CO<sub>3</sub>+31.5 mol% Na<sub>2</sub>CO<sub>3</sub>+25 mol% K<sub>2</sub>CO<sub>3</sub> (Li-Na-K). The carbon and carbonate mixtures were kept at 200 °C under vacuum prior to use. The mixed ratios of carbon and Li-Na carbonates were 5 g : 5 g, 5 g : 20 g, and 20 g : 20 g.

The carbon and carbonate mixture was held in an alumina crucible that was placed in a metal cylinder-type container with a volume of 1.25 L (Fig. 1), ca. 10 cm inner diameter and ca. 30 cm in length. The metal container was gas sealed and settled in a circular electric heater. The temperature of the metal container was controlled in the range 650-800 °C, and was measured with a K-type

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**Fig. 1. Experimental apparatus for carbon gasification.**

- |  |                      |
|--|----------------------|
| a. N <sub>2</sub> or air inlet port          | h. Thermal insulator |
| b. N <sub>2</sub> or air direct inlet valve  | i. Electric heater   |
| c. Glass flask                               | j. Metal container   |
| d. Electric heater                           | k. Water jacket      |
| e. Steam inlet port                          | l. Gas sampling port |
| f. Line heater                               | m. Mass cylinder     |
| g. Carbon- and carbonate-containing crucible | n. Water bath        |

thermocouple. The amount of evolved gas was measured by using the water substitution method; thus, cumulative gas amounts were obtained. The evolved gas was sampled by a gas syringe (250  $\mu$ l) at the gas outlet of the container and its composition was measured by gas chromatography (GC, HP model 5890II). The column material of the GC was Porapak Q and the detector was TCD. The metal container was initially filled with N<sub>2</sub> gas.

The carbon oxidation behavior was also measured by thermogravimetric analysis (TGA, Mettler Toledo 851). The temperature was increased by 20  $^{\circ}\text{C min}^{-1}$  under N<sub>2</sub> purge conditions.

For carbon steam reforming, several carbon-to-carbonate ratios were prepared: 20 g + 0 g, 20 g + 1 g, 20 g + 2 g, 20 g + 10 g, and 20 g + 20 g. The carbonate was 62 mol% Li<sub>2</sub>CO<sub>3</sub>+38 mol% K<sub>2</sub>CO<sub>3</sub> eutectics. The carbon and carbonate mixtures were placed in an alumina crucible and 0.2 L min<sup>-1</sup> N<sub>2</sub> or air was purged through a water bubbler at 85  $^{\circ}\text{C}$ . Thus, about 0.3 L min<sup>-1</sup> of steam was supplied to the mixture. The temperature and gas sampling method were the same as in the experiment without H<sub>2</sub>O.

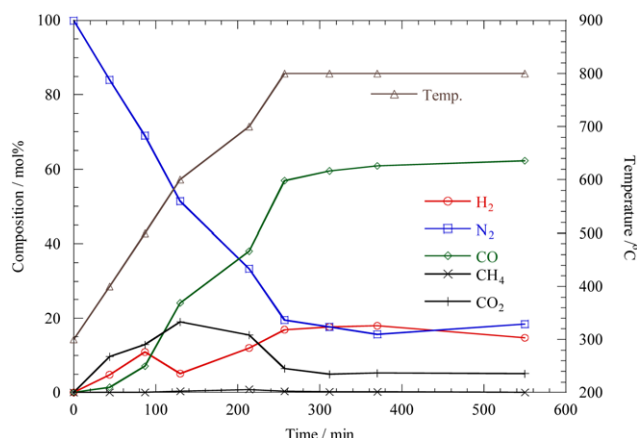
## RESULTS AND DISCUSSIONS

### 1. Gasification of Carbon with Carbonate under N<sub>2</sub> Condition

Fig. 2 shows compositions of the gases evolved by the 5 g carbon and 5 g Li-Na carbonate mixture with increasing temperature. No gas generation was observed up to 300  $^{\circ}\text{C}$ . However, at 500  $^{\circ}\text{C}$ , CO<sub>2</sub>, CO, and H<sub>2</sub> were produced. Among these gases CO<sub>2</sub> was dominant. Indeed, as carbonates melt at around 500  $^{\circ}\text{C}$ , carbon and carbonate may not have undergone any chemical reactions below 500  $^{\circ}\text{C}$ . Thus the CO<sub>2</sub> would be the result of the self-decomposition of carbonate (Eq. (4)) [8].



Another possibility is that carbon oxidation occurred via the functional oxygen species in the carbon [1]. Since carbon is a porous



**Fig. 2. Gas compositions with respect to temperature and time for the 5 g carbon and 5 g Li-Na carbonate mixture.**

material, a significant amount of oxygen species would have been present in the carbon even though it was dried. In another experiment of this work, the CO<sub>2</sub> concentration only with 5 g carbon in the crucible at 500  $^{\circ}\text{C}$  was ca. 7 mol%. This indicates that some CO<sub>2</sub> was produced from the oxygen species on the carbon. The latter possibility is more acceptable because carbonate exists in a solid state below 500  $^{\circ}\text{C}$  and its decomposition is less plausible.

About 10 mol% of H<sub>2</sub> was observed, as shown in Fig. 2. This gas might have been discharged out of the carbon that was initially included during carbonization. Another possibility is that it was produced via the water-gas-shift reaction (Eq. (5)).



However, the carbon was dried and the cell was purged by N<sub>2</sub> gas. Thus the remaining H<sub>2</sub>O would have been too small to generate such a high H<sub>2</sub> concentration.

A very small amount of CH<sub>4</sub> evolved from the carbon. In the experiment using carbon only, CH<sub>4</sub> was observed as the temperature increased, although only at a low concentration. Thus, it is plausible that CH<sub>4</sub>, which initially existed in the carbon, was derived from the carbon.

Above 600  $^{\circ}\text{C}$ , CO generation became dominant. At such temperatures, the carbonate melts and the chemical reaction between the carbon and carbonate shown in Eq. (1) may take place. On the other hand, the reverse Boudouard reaction (Eq. (2)) is also activated at such temperatures [6]. Contrasting behaviors were observed for CO and CO<sub>2</sub>: the CO concentration increased, whereas the CO<sub>2</sub> concentration decreased with temperature. This indicates the following two possibilities. With reaction (1) CO generation leads to the accumulation of oxide in the carbonate melts, and is regenerated by CO<sub>2</sub> recombination, the reverse reaction of Eq. (4). Reportedly, CO<sub>2</sub> recombination is much faster than the reaction of Eq. (1) [6]. Thus, CO<sub>2</sub> is consumed by the reverse reaction of Eq. (4) and its concentration is reduced. Another possibility involves the consumption of CO<sub>2</sub> by the reverse Boudouard reaction of Eq. (2). The reaction (2) with alkali carbonates such as Na<sup>+</sup> and K<sup>+</sup> is much faster than the intermolecular redox reaction of Eq. (1) [6]. Thus, CO<sub>2</sub> is consumed, and the CO concentration increases correspondingly.

The generation of CO also reduced the N<sub>2</sub> concentration in the

metal container. However, at a fixed temperature of 800 °C, all gas concentrations showed constant values. This indicates that gas evolution is halted at this temperature, and it also implies that gas generation is strongly dependent on temperature. The gas concentrations at 800 °C were as follows: CO, 62.2 mol%; H<sub>2</sub>, 14.7 mol%; and CO<sub>2</sub>, 5.7 mol%. The theoretical equilibrium constant of the reverse Boudouard reaction is about 7.0 at this temperature. The measured equilibrium constant of the Boudouard reaction was 6.8, which is very close to the theoretical value. This behavior indicates that the Na<sub>2</sub>CO<sub>3</sub> in the carbonates enhanced CO production and that the rate reached the thermodynamic value of the reverse Boudouard reaction. The results also indicate that carbon with carbonate spontaneously produces CO at the temperature of 800 °C.

Fig. 3 shows the amounts of gas accumulated with increasing temperature. This was measured by water substitution, and thus is a total amount. Although CO<sub>2</sub> has a degree of solubility in water, the volume decrease due to CO<sub>2</sub> dissolution was ignored. Up to 800 °C gas generation rose monotonically. As shown in Fig. 2, CO<sub>2</sub> and H<sub>2</sub> were the main components below 500 °C, but CO dominated over this temperature. At 800 °C no further gas generation was observed. Since CO<sub>2</sub> gas was not supplied to the reactor, the recombination of oxide ion (O<sup>2-</sup>) with CO<sub>2</sub>, which is the reverse reaction of

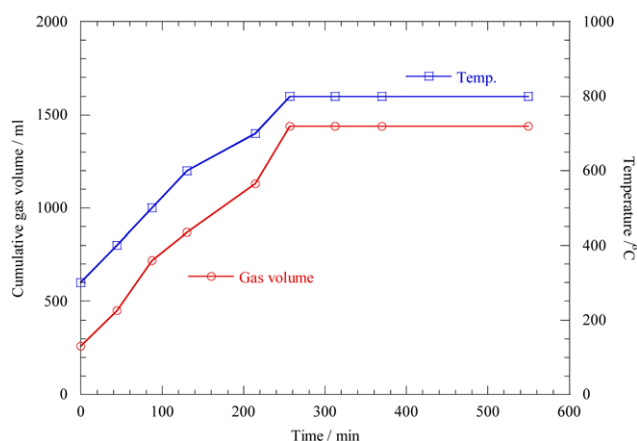


Fig. 3. Accumulated gas volume from the 5 g carbon and 5 g Li-Na carbonate mixture with increasing temperature.

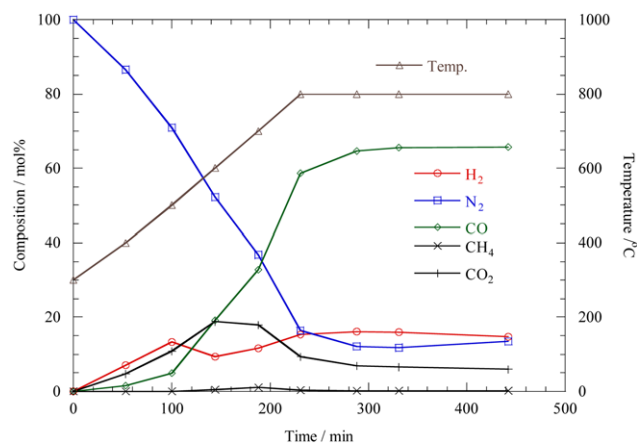


Fig. 4. Gas compositions with respect to temperature and time for 5 g carbon and 20 g Li-Na carbonate.

Eq. (4), and the reaction of Eq. (1) could not continue. Given the lack of CO<sub>2</sub> the reverse Boudouard reaction (Eq. (2)) was also unavailable. This behavior is in line with the results of a previous study that a helium gas environment did not allow continuous CO generation in the Li<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> conditions [6].

Fig. 4 shows the gas compositions obtained with 5 g carbon and 20 g Li-Na carbonate as temperature increased. The behaviors of composition were very similar to those in Fig. 2. Below 500 °C, CO<sub>2</sub> and H<sub>2</sub> were the main components, but CO became dominant over this temperature. At 800 °C, the compositions became constant, indicating that carbon oxidation could not continue. Although the amounts of carbonate were four times higher than those in Fig. 2, very similar behaviors of composition were observed. A previous study reported that the catalytic effect of alkali carbonate does not depend on the amount beyond a certain value [6]. The CO<sub>2</sub> compositions (in Fig. 2 and Fig. 4) at 500 °C were 12.9 and 10.8 mol%, respectively. Regardless of the difference in the amount of carbonate, similar CO<sub>2</sub> compositions were obtained. This indicates that CO<sub>2</sub> generation at this temperature is strongly dependent on the oxidation of carbon by the oxygen species inside the porous carbon rather than carbonate decomposition via Eq. (4). The gas compositions at 800 °C were CO, 65.7 mol%; H<sub>2</sub>, 14.6 mol%; and CO<sub>2</sub>, 6.0 mol%. The experimental equilibrium constant of Eq. (2) was 7.19, which is very close to the theoretical value of 7.0.

Fig. 5 shows the amount of gas accumulated with increasing temperature. This rose with temperature up to 800 °C. The total amount of gas at 800 °C was 1.63 L, which was close to 1.44 L of Fig. 3. Thus, gas generation does not depend on the amount of carbonate in this experimental range.

Fig. 6 shows the gas compositions produced by the 20 g carbon and 20 g Li-Na carbonate mixture as temperature increased. In particular, the CO<sub>2</sub> composition around 500 °C was 29 mol%, which was much higher than that at 5 g carbon, as shown in Figs. 2 and 4. Therefore, the CO<sub>2</sub> composition at 500 °C was strongly dependent on the amount of carbon. This strongly suggests that the carbon reacts with functional oxygen species in the carbon, resulting in CO<sub>2</sub> generation, although the carbon was stored in vacuum at 200 °C.

The CH<sub>4</sub> composition at 500 °C was 3.8 mol%, which is very

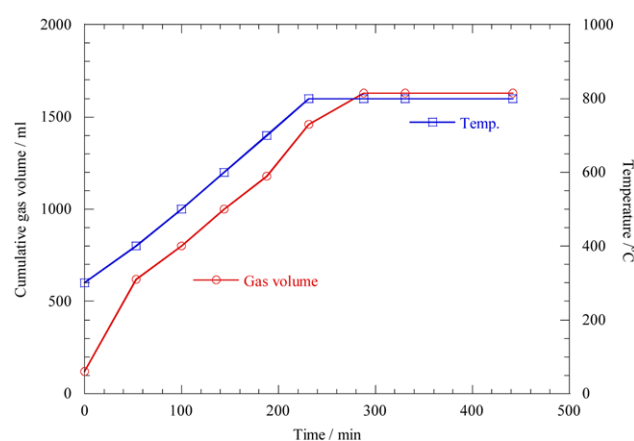


Fig. 5. Accumulated gas volume from the 5 g carbon and 20 g Li-Na carbonate mixture.

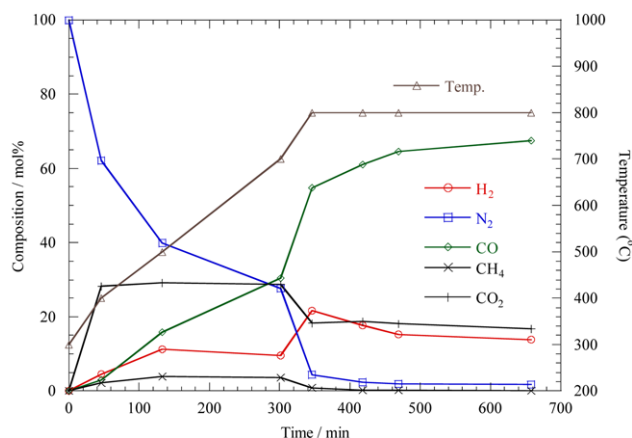


Fig. 6. Gas compositions with respect to temperature and time for 20 g carbon and 20 g Li-Na carbonate.

high compared with the value of zero in Figs. 2 and 4. The high  $\text{CH}_4$  composition is due to the increasing amount of carbon. One possibility for the  $\text{CH}_4$  generation is the chemical reaction of carbon with hydrogen (Eq. (6)):



The equilibrium constant of Eq. (6) was about 2.2 at 500 °C, so  $\text{CH}_4$  formation is theoretically possible in such conditions. However, if the reaction (6) is active at 500 °C,  $\text{CH}_4$  should be generated in the 5 g carbon conditions because solid carbon has one of activity. The zero composition of  $\text{CH}_4$  in Figs. 2 and 4 indicates that reaction (6) may not be active in this condition. Another possible reason is the escape of  $\text{CH}_4$  from the carbon. The  $\text{CH}_4$  was initially stored in the carbon during carbonization. The ratio of  $\text{CH}_4$  to carbon supports this hypothesis.

With increasing temperature CO increased and  $\text{CO}_2$  decreased. Combinations of reaction (1) and (4) may be responsible for this behavior. The gas concentrations at 800 °C were CO, 67.5 mol%;  $\text{H}_2$ , 13.9 mol%; and  $\text{CO}_2$ , 16.8 mol%. It should be noted that the  $\text{CO}_2$  composition was about triple those in Figs. 2 and 4. Although the reason for this is not yet clear, a relatively large amount of  $\text{CO}_2$

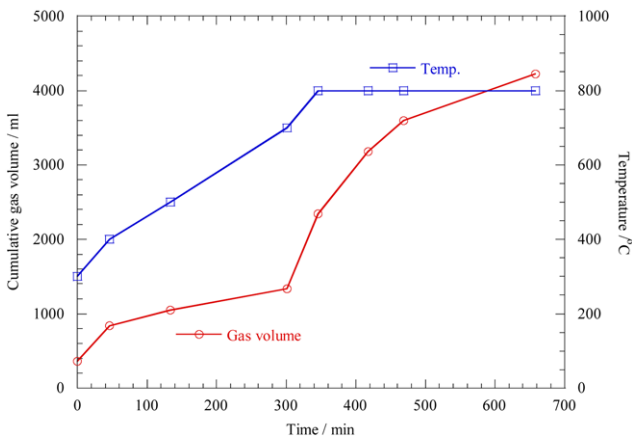


Fig. 7. Accumulated gas volume from the 20 g carbon and 20 g Li-Na carbonate mixture.

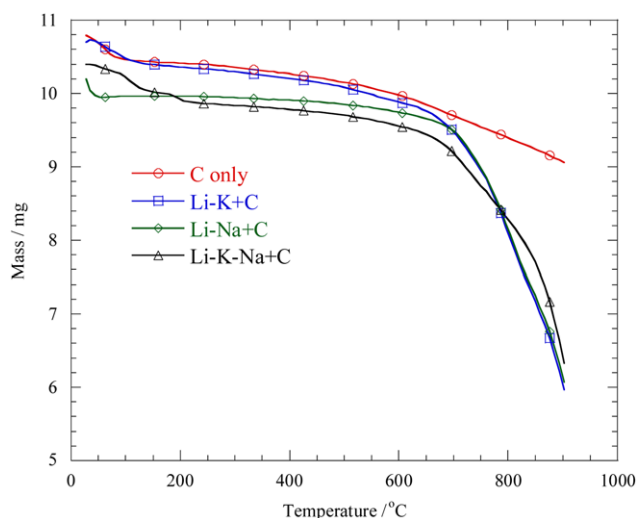


Fig. 8. TGA results of carbon and various carbon-carbonate mixtures under an  $\text{N}_2$  environment.

is produced at higher carbon loading during CO generation.

Fig. 7 shows the gas produced by the 20 g carbon and 20 g carbonate mixtures. Over 700 °C steep increases in the amounts of gas were observed, mostly due to CO generation, as shown in Fig. 6. CO generation thus has a positive relation with carbon amount over the temperature.

Fig. 8 shows the TGA results of the carbon and carbon-carbonate mixtures under an  $\text{N}_2$  environment. Three carbon and carbonate mixtures, C : Li-K=1 : 1 mass ratio, C : Li-Na=1 : 1 mass ratio, and C : Li-Na-K=1 : 1 mass ratio, were employed. The carbon/carbonate mixtures showed a steep decrease in mass over 700 °C, whereas carbon did not show any major decrease. This indicates that carbon is hardly oxidized over 700 °C but that carbon with carbonate is significantly oxidized over this temperature regardless of composition. All mixtures commenced carbon oxidation at around 700 °C and the slopes of mass decrease were very similar. Indeed, the melting point of Li-Na-K carbonate is ca. 100 °C lower than that of Li-K and Li-Na carbonates. Thus different mass decrease behavior could

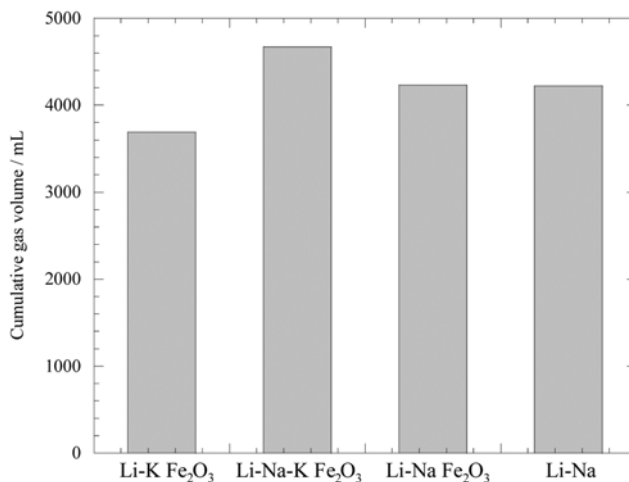


Fig. 9. Cumulative gas volume with 4 g of  $\text{Fe}_2\text{O}_3$  in 20 g carbon and 20 g of various carbonates at 800 °C.

be expected. However, the similar slopes indicate that the carbon oxidation behavior is very similar among the carbonates. The TGA and gas concentration analysis gave consistent results regarding the carbon oxidation temperature of 700 °C.

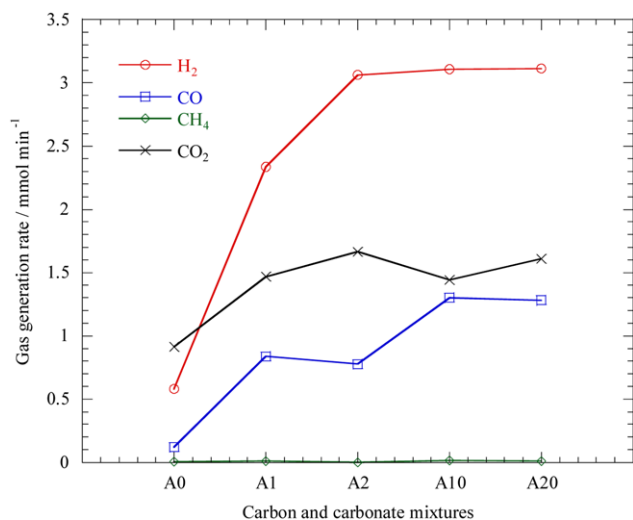
Wu et al. reported that iron oxide behaved as a catalyst for carbon oxidation [9]. In the current study, 4 g of  $\text{Fe}_2\text{O}_3$  was added to 20 g of carbon and 20 g of carbonate mixture. Three carbonate compositions were employed. Fig. 9 shows the total accumulated gas amounts up to 800 °C with respect to composition. About 65% of the total gas was composed of CO according to Fig. 6. Thus the amount of gas is a measure of the catalytic effect of  $\text{Fe}_2\text{O}_3$ . As shown in this figure, the gas amounts produced by the carbonate species were within the ranges of error regardless of  $\text{Fe}_2\text{O}_3$  addition, which indicates that  $\text{Fe}_2\text{O}_3$  does not have a catalytic effect on carbon oxidation in the carbon/carbonate mixtures. Table 1 summarizes gas compositions from  $\text{Fe}_2\text{O}_3$  added carbon and carbonate mixtures. The Li-Na-K carbonate shows rather higher CO composition compared with others, but insignificant differences in the gas generation behaviors are admitted among the carbonate compositions.

## 2. Gasification of Carbon with Steam

According to the reaction of Eq. (3) carbon can be reformed to  $\text{H}_2$  and CO by steam. Fig. 10 shows the compositions of the gases produced from the carbon and steam with various amounts of carbonate at 800 °C. A fixed amount of  $\text{N}_2$  (0.2 L  $\text{min}^{-1}$ ) was supplied through an 85 °C water bubbler, so the gas flow contained 0.3 L

**Table 1. Gas compositions measured from  $\text{Fe}_2\text{O}_3$  added carbon and carbonate mixtures via gas chromatography**

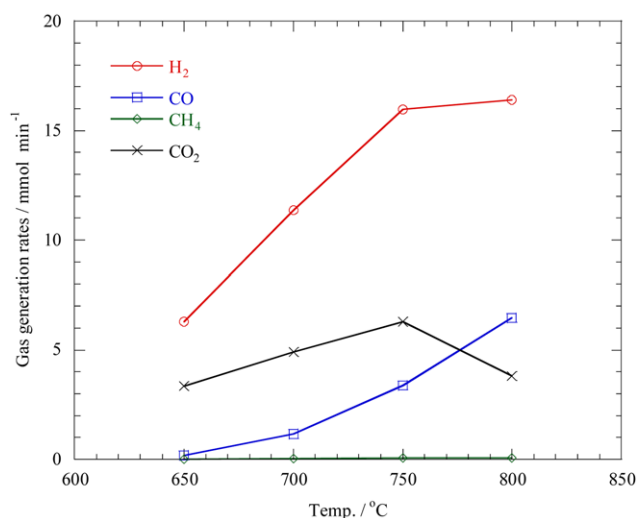
Gas species	Li-K/mol%	Li-Na/mol%	Li-Na-K/mol%
$\text{H}_2$	20.5	18.7	17.0
$\text{N}_2$	1.7	1.4	2.1
CO	62.7	67.8	70.9
$\text{CH}_4$	0.5	0.4	0.4
$\text{CO}_2$	14.6	11.7	10.5



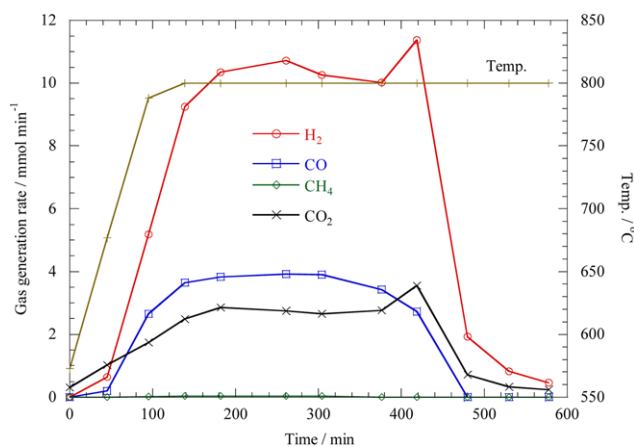
**Fig. 10. Gas generation rates with 0.2 L  $\text{min}^{-1}$   $\text{N}_2$  through 85 °C water into various amounts of Li-K carbonate and 20 g of carbon mixtures at 800 °C. A0, 0 g of carbonate; A1, 1 g; A2, 2 g; A10, 10 g; A20, 20 g.**

$\text{min}^{-1}$   $\text{H}_2\text{O}$ . The amounts of carbonate added to 20 g of carbon were 0, 1, 2, 10, and 20 g, respectively. Since  $\text{N}_2$  is inert in these conditions, the gas evolution rate could be calculated from the composition ratio between  $\text{N}_2$  and other gases. When CO and  $\text{H}_2$  are produced by the reaction of Eq. (3), the gases generate  $\text{CO}_2$  by the water-gas-shift reaction of Eq. (5). At 0 g of carbonate,  $\text{CO}_2$  is the dominant species among  $\text{H}_2$ ,  $\text{CO}_2$ , CO, and  $\text{CH}_4$ . However, when the carbonates are added,  $\text{H}_2$  is the dominant species and CO also rises. Above 2 g of carbonate, the  $\text{H}_2$  composition reaches to a certain value and composition of other gases also converges. Thus about 10 wt% of carbonate to carbon has a sufficient catalytic effect on carbon steam reforming. The results indicate that carbonate addition increases the  $\text{H}_2$  and CO production rate and that carbon steam reforming produces  $\text{H}_2$  and CO species.

Fig. 11 shows the effect of temperature on carbon steam reforming with 20 g Li-K carbonate, 20 g carbon, and 0.2 L  $\text{min}^{-1}$   $\text{N}_2$  through an 85 °C water bubbler. At 650 °C CO generation is very low as is that of  $\text{H}_2$ . With increasing temperature,  $\text{H}_2$  and CO increase notice-



**Fig. 11. Gas generation rates at various temperatures with 0.2 L  $\text{min}^{-1}$   $\text{N}_2$  through 85 °C water into 20 g Li-K carbonate and 20 g carbon.**



**Fig. 12. Gas generation rates up to 800 °C with 0.2 L  $\text{min}^{-1}$   $\text{N}_2$  through 85 °C water into 20 g carbon and 20 g Li-K carbonate.**



ably, while  $\text{CO}_2$  is reduced at 800 °C. The equilibrium constant of the water-gas-shift reaction (Eq. (5)) decreases as temperature rises. Reduction of the constant may explain the decrease in  $\text{CO}_2$  generation at 800 °C. Consequently,  $\text{H}_2$  and  $\text{CO}$  generation increases with temperature and is a strong function of temperature.

Fig. 12 shows the gas generation rates with respect to time for 20 g Li-K, 20 g C, and 0.2 L  $\text{min}^{-1}$   $\text{N}_2$  through an 85 °C water bubbler up to 800 °C. At about 100 min gas generation reaches a steady state.  $\text{H}_2$  is the most generated species, and slightly more  $\text{CO}$  is generated than  $\text{CO}_2$ . This is in line with the results shown in Fig. 11. Gas generation continues for about 10 hours. After the experiment, no carbon was observed in the alumina crucible and only white carbonates remained, indicating that the solid carbon was totally oxidized to a gaseous product.

The above results demonstrate that  $\text{N}_2$  is an appropriate steam carrier in carbon steam reforming. The possibility of the substitution of  $\text{N}_2$  with air was also investigated. Fig. 13 shows the gas compo-

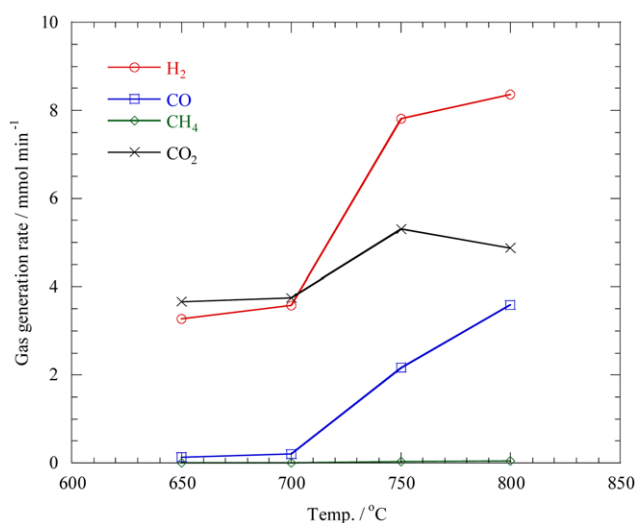


Fig. 13. Gas generation rates at various temperatures with 0.2 L  $\text{min}^{-1}$  air through 85 °C water into 20 g Li-K carbonate and 20 g carbon.

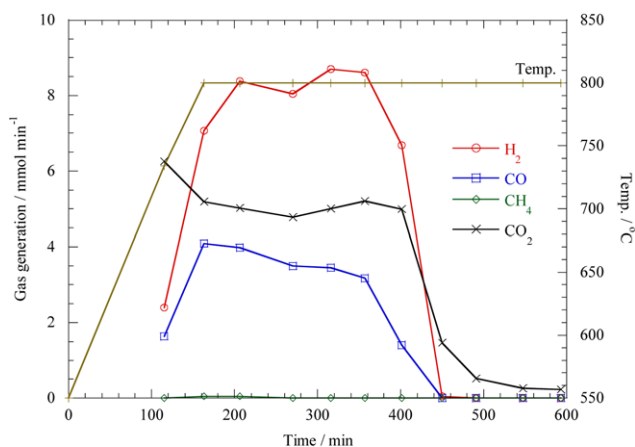


Fig. 14. Gas generation rates up to 800 °C with 0.2 L  $\text{min}^{-1}$  air through 85 °C water into 20 g carbon and 20 g Li-K carbonate.

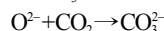
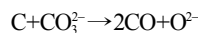
sitions with 0.2 L  $\text{min}^{-1}$  air through 85 °C water for the 20 g C and 20 g Li-K carbonate at various temperatures. Air contains about 80%  $\text{N}_2$ , and thus other gas flow rates could be measured. At lower temperatures  $\text{CO}_2$  is the dominant species because  $\text{H}_2$  and  $\text{CO}$  production is relatively small and they are oxidized to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  by the oxygen in air. However,  $\text{H}_2$  and  $\text{CO}$  generation greatly increases above 700 °C. At such temperatures, carbon steam reforming must be highly activated. On the other hand, the  $\text{CO}_2$  flow rate is relatively invariant. This indicates that  $\text{CO}_2$  generation is determined by the amount of  $\text{O}_2$  in the air.

Fig. 14 shows the gas generation rates with 0.2 L  $\text{min}^{-1}$  air through an 85 °C water bubbler for the 20 g C and 20 g Li-K carbonate up to 800 °C. Unlike in  $\text{N}_2$  flow, the  $\text{CO}_2$  generation rate is higher than that of  $\text{CO}$ . On the other hand,  $\text{H}_2$  shows the highest rate of generation, indicating that air as a steam carrier produces  $\text{H}_2$  as the dominant species, and that the gas species have relatively constant values. After gas generation ceased, only white carbonates were observed in the crucible. The carbon fuel was totally oxidized.

## CONCLUSIONS

Carbon oxidation with alkali carbonates was investigated by analyzing compositions and measuring total gas evolution. The carbon-to-carbonate ratio, temperature, carbonate compositions, catalyst effect, and steam addition were considered. The investigation led to the following conclusions:

1. Carbon is oxidized to  $\text{CO}$  in the presence of carbonate according to the following reactions:



2.  $\text{CO}$  generation is strongly dependent on the amount of carbon rather than carbonate.

3.  $\text{CO}$  generation is activated over 700 °C.

4. Carbon oxidation behavior is barely influenced by the carbonate species.

5.  $\text{Fe}_2\text{O}_3$  as a catalyst had a negligible catalytic effect on carbon oxidation.

6. The supply of steam to a high temperature carbon and carbonate mixture resulted in  $\text{H}_2$  and  $\text{CO}$  generation, referred to as carbon steam reforming.

7. Alkali carbonate catalyzed carbon steam reforming.

8. Carbon steam reforming was successfully carried out with  $\text{N}_2$  and air as the steam carrier.

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