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Carbon dioxide absorption mechanisms of sodium added to calcium oxide at high temperatures

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Abstract

To apply the CO_2 absorber at about 1000 °C for integrated coal gasification combined cycle (IGCC) furnace, the reactions of calcium oxide and CO_2 at high temperatures was examined. Calcium carbonate reacts with sodium hydrogen carbonate below 200 °C and forms sodium–calcium complex carbonate. The sodium–calcium complex carbonate melts at 813 °C, and the carbon dioxide absorption and discharge reversible reactions of calcium-oxide takes place via liquid at around 1000 °C. Sintering of calcium oxide at high temperature has been successfully avoided by the addition of sodium.

Keywords: C: Chemical properties; D: Alkali oxides; E: Thermal application

1. Introduction

In recent years, attention has been seriously paid to the reduction of carbon dioxide (CO_2) emissions. Most greenhouse gases released from industries in the atmosphere have a bad influence on global warming [1]. The separation of CO_2 gas that has been discharged from industrial field and/or power plant in high concentration as exhaust gases and its recovery is inevitable. There are some useful methods for the separation and the recovery of CO_2 gas from exhaust gases, such as adsorption in the solvent [2], segregation by ceramics films [3] and so on. In the separation method proposed by Matsuyama et al. [2], the temperature of exhaust gas need to be cooled down to temperature below 200 °C. Hence, consideration of effective use of this method for the separation of high temperature exhaust gases is inefficient [4]. Therefore, it is advantageous in thermal efficiency that the separation and the recovery of CO_2 gas from exhaust gas perform at high temperatures.

Lithium containing complex oxides, such as, lithium silicates or lithium zirconate, that show reversible absorption and discharge of CO_2 gas at high temperatures, are candidate materials for the segregation and the recovery of CO_2 gas at high temperatures [5,6]. However, the abundance of lithium element is very low and expensive as compared with other alkali metal elements such as sodium and potassium or alkaline-earth metal elements such as magnesium and calcium. Hence, it is difficult for the practical use of large amounts of lithium complex oxides to separate CO_2 gas at power plant or industrial field. And also the absorption of CO_2 gas of lithium silicates or lithium zirconate occur below 800 °C.

Integrated coal gasification combined cycle (IGCC) system is a promising system of electricity generation in near future because of its high thermal efficiency. The temperature of coal gasification occurs at 2000 °C. From the endothermic reaction by adding gasification agent, the temperature of the gases cool down to 1100 °C at the outlet of the gasification reactor [7].

Search for high efficiency CO_2 absorption materials which consist of sodium, potassium, magnesium, calcium complex oxides, operating at high temperatures of about 1000 °C, is prime important. In this case, magnesium and calcium oxides easily sinter at high temperatures, so a restrain mechanism of the sintering of magnesium and calcium oxides will be required for a long time use.

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In this paper, CO_2 absorption reaction of calcium oxide at high temperatures discussed.

2. Experimental

High purity $CaCO_3$ (99.9% purity, Kojundo Chemical Lab Co., Ltd.) and $NaHCO_3$ (99.5% purity, Wako Pure Chemical Industries, Ltd.) were used as the starting materials. The required amounts of respective chemicals were mixed in the agate mortar by proper ratio. Table 1 shows the compositions of mixed powders in this study. Thermal analyses for these mixed powders were carried out up to 1200 °C by thermo-gravimetric apparatus (model: Thermo Plus TG 8120, Rigaku Co., Ltd) in a flowing CO_2 gas (5 ml/min) atmosphere, at a heating and cooling rate of 10 K/min.

The identification of the phases was examined by powder X-ray diffraction method using X-ray diffractometer (model: RINT 2000, Rigaku Co., Ltd.).

3. Results and discussion

Fig. 1a shows the result of differential thermal analysis (DTA) of pure $CaCO_3$ and Fig. 1b shows change in weight during cyclic thermal test from 300 to 1200 °C, carried out for six cycles. From DTA curve (Fig. 1a), it is recognized that the temperature beginning of the CO_2 release is 923 °C during heating process and the beginning of CO_2 absorption is 877 °C during cooling process, indicating that $CaCO_3$ reacts with CO_2 at 900 °C in CO_2 atmosphere. It should be noted that this reaction is a reversible reaction.

Table 1
The composition of each sample

Sample name	$CaCO_3$:$NaHCO_3$ (mole)
Na-1.2	1:0.012
Na-30.5	1:0.305
Na-93.2	1:0.932

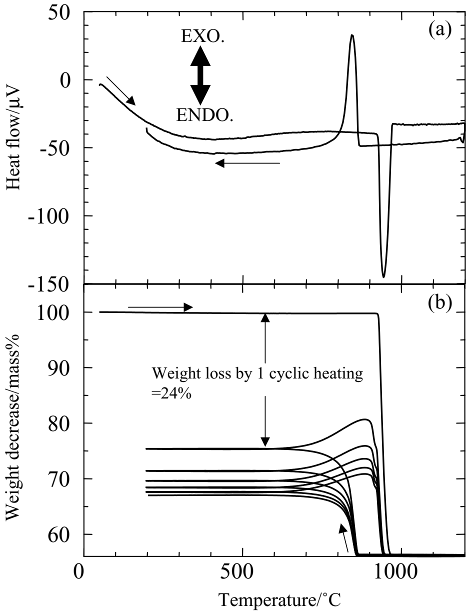

Fig. 1. (a) DTA curve and (b) TG curve for $CaCO_3$.

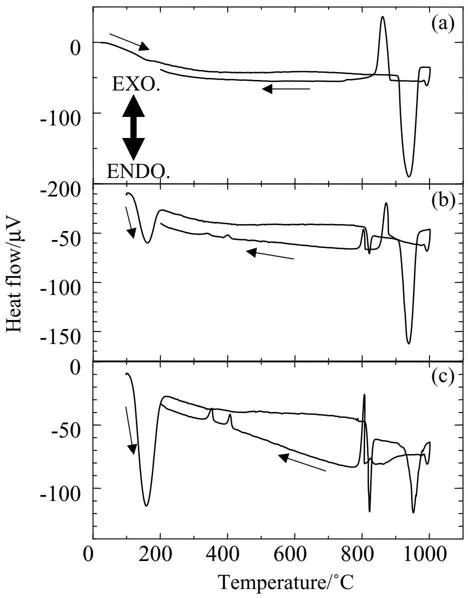

Fig. 2. DTA curves of (a) Na-1.2, (b) Na-30.5 and (c) Na-93.2 samples, respectively.

After the discharge of CO_2 gas at about 900 °C, the weight of calcium oxide (CaO) is unchanged above 900 °C, as can be shown in Fig. 1b. In this experimental condition, the weight loss at about 600 °C during the first cycle of heat treatment is 24 wt.%. Large CaO particles were formed by sintering at about 900 °C. CO_2 absorption reaction occurs at the surface of CaO particle during cooling process, so that the growth of CaO particle brings the shrinking of the amount CaO that can not contribute to the reaction of CO_2 absorption.

Fig. 2a–c show the DTA curves of Na-1.2, Na-30.5 and Na-93.2 samples, respectively, from room temperature to 1000 °C. Fig. 3 shows the powder X-ray diffraction

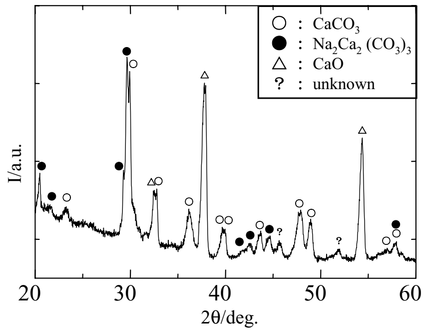

Fig. 3. Powder X-ray diffraction pattern of Na-30.5 sample after thermal analysis.

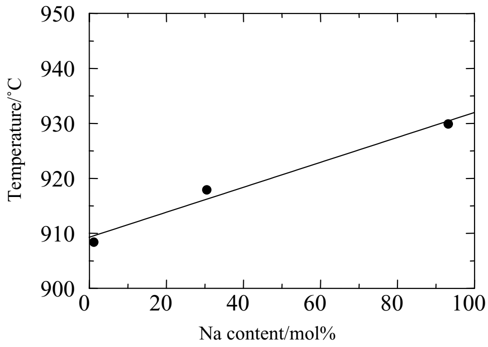

Fig. 4. CO_2 discharging temperatures of each samples.

pattern of Na-30.5 sample after DTA measurement. The formation of sodium–calcium complex carbonate $Na_2Ca_2(CO_3)_3$ is recognized from Fig. 3.

The endothermic reaction, which occurs about 200 °C in Fig. 2, has been understood as the formation of Na_2CO_3 by the decomposition of $NaHCO_3$ and simultaneously the formation of $Na_2Ca_2(CO_3)_3$ by Na_2CO_3 and $CaCO_3$ reaction. In Fig. 2b and c, endothermic and exothermic peaks are formed at 813 °C, and this is attributed to the melting of complex carbonate $Na_2Ca_2(CO_3)_3$ [8].

The temperature of CO_2 release from $CaCO_3$ slightly increases with increasing amount of sodium concentration as shown in Fig. 4. And also by increasing the sodium concentration, exothermic reaction peak corresponding to CO_2 absorption at about 900 °C at cooling step decreases and in the case of Na-93.2 (Fig. 2c), exothermic reaction peak disappeared.

Fig. 5 shows the weight changes for Na-30.5 sample. There is an initial weight loss corresponding to the formation of Na_2CO_3 by decomposition of $NaHCO_3$, in the temperature range from room temperature to 200 °C. From 200 to 800 °C, there is no change in weight. However, it is observed that the weight decreases and increases at about 900 °C, which corresponds to the release of CO_2 gas from $CaCO_3$ and absorption of CO_2 gas by CaO. Similar result has been obtained also for Na-1.2 and Na-93.2 samples (not shown here).

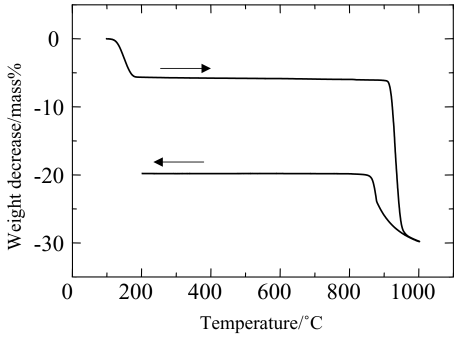

Fig. 5. TG curve for Na-30.5 sample.

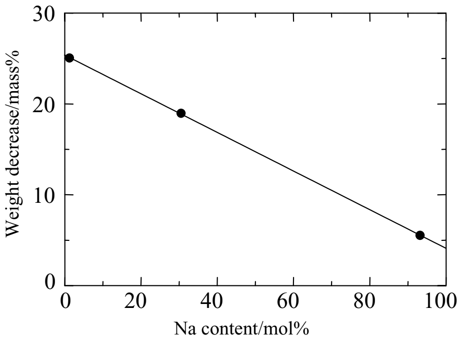

Fig. 6. Weight loss by one cyclic thermal analysis for each samples.

The weight loss measured at 600 °C after one thermal cycle has been plotted against the addition of sodium in Fig. 6. The amount of weight loss corresponding to the sintering of CaO at above 900 °C decreases with increasing sodium content, i.e. by adding sodium to $CaCO_3$, the sintering of CaO at high temperature was successfully avoided. On the other hand, the amount of CO_2 absorption slightly decreases with sodium content (Fig. 7).

From above results, the avoid of weight loss, i.e. the restrain of the sintering of CaO mechanism at high temperatures can be discussed as follows. $NaHCO_3$ added to the $CaCO_3$ system forms complex carbonate $Na_2Ca_2(CO_3)_3$ below 200 °C in CO_2 atmosphere. When $Na_2Ca_2(CO_3)_3$ melts at below 900 °C, $CaCO_3$ particle will be surrounded by $Na_2Ca_2(CO_3)_3$ liquid and hence, the CO_2 gas release from $CaCO_3$ and the CO_2 gas absorption by CaO reactions must occur through the liquid. CO_2 release and absorption occurring through the $Na_2Ca_2(CO_3)_3$ liquid is the rate-determining step, so that the beginning CO_2 release from $CaCO_3$ temperatures increases with increasing amount of liquid, namely the amount of $Na_2Ca_2(CO_3)_3$ phase, as shown in Fig. 4. In the CO_2 absorption reaction, once CO_2 gas enters the liquid, the absorption of CO_2 gas in the liquid will be the rate-determining step, so that the CO_2 absorption takes for a long duration of time. This is the reason for the peak corresponding to CO_2 absorption, which decreases with increasing sodium content as shown Fig. 2. Before particle growth by sintering, large amount of $CaCO_3$ would be

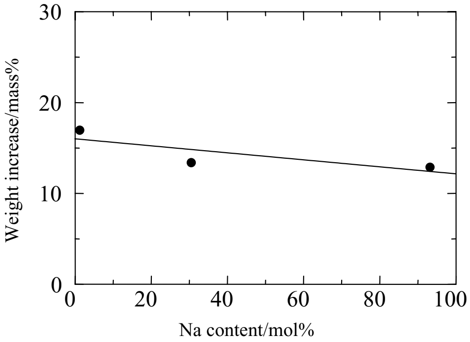

Fig. 7. Weight increase by CO_2 absorption for each samples.

surrounded by liquid $Na_2Ca_2(CO_3)_3$ phase, then the sintering of CaO at above 900 °C would be successfully restrained. The amount of $CaCO_3$ surrounded by liquid phase increases by increasing the amount of $Na_2Ca_2(CO_3)_3$ phase, so that the influence of sintering of CaO, namely, the weight loss at 600 °C decreases by increasing sodium content.

4. Conclusion

The CO_2 discharge and absorption reaction of sodium added to $CaCO_3$ at about 900 °C occur through $Na_2Ca_2(CO_3)_3$ liquid phase. $CaCO_3$ particle is surrounded by the liquid phase, so the sintering of CaO at high temperatures could be successfully avoided. Therefore, in the development of CO_2 absorptive materials consisting of calcium oxide or calcium complex oxides operating at high temperatures, it is effective to restrain the sintering of CaO by combining with materials that have melting point just below 900 °C.

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