A Novel CO_2 Absorbents using Lithium-containing Oxides

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Abstract

A series of lithium containing oxides immediately reacts with ambient CO_2 up to 700°C. The products react and return reversibly to the oxides at temperatures above 700°C. The capacity of the absorption surpasses that of previous CO_2 absorbents by a factor of ten. Utilizing these absorbents, the possibility of a CO_2 separation system which operates at around 500°C is suggested. It is generally believed that a CO_2 separation process operable at temperatures beyond 500°C has a special benefit of small energy penalty, because the separation can be achieved directly during the fuel reforming process.

1. Introduction

Since the Kyoto COP3 meeting, general interest for the reduction of carbon dioxide (CO_2) emission has been increasing. However, concrete actions for the reduction are hardly proceeding. It is because CO_2 emission and energy production by fossil fuel combustion are closely connected, and the reduction might cause political problems which seriously affect economy of each country.

Present technical efforts for the reduction can be summarized into 3 categories of "improvement of energy conversion efficiency", " development of new energy sources" and "recovery and isolation of CO_2". Among these categories, technical development relating to recovery and isolation of CO_2 has been intensively promoted in recent years, recognizing that the reduction is not sufficient by improvement of energy efficiency and that development of new energy sources seems to be considerably difficult in near future. How to separate CO_2 from exhaust gas of power plant with minimum energy penalty and to isolate it from atmosphere are the key points of this technology.

2. Benefit of CO_2 separation at high temperature

In order to recover CO_2 efficiently, it is preferable to separate it at the highest possible concentration. The proposed method based on this basic concept is CO_2 separation from fuel gas, not from flue gas. There is a fuel gas containing up to 50% CO_2 at fuel reforming process. Some reports describe that the energy penalty of CO_2 separation from fuel gas would be reduced by half. On the other hand, there is no practical technology to recover CO_2 from high temperature gas.

3. Novel CO_2 absorbent

In the process of fuel cell development, we found reversible reaction of lithium zirconate (Li_2ZrO_3) at high temperature. The reaction is represented by Eq. 1. Lithium zirconate changes to zirconium oxide (ZrO_2) reacting with CO_2 at around 500^oC and the reaction changes the direction above 700^oC.

$$Li_2ZrO_3 + CO_2 = ZrO_2 + Li_2CO_3 \qquad \text{Eq.1}$$

Since this reaction is reversible, lithium zirconate would be a regenerable CO_2 absorbent at high temperature. On the basis of this finding, we have studied similar reactions between lithium-containing oxides, *e.g.*, lithium aluminate ($LiAlO_2$), lithium ferrite ($LiFeO_2$), lithium titanate (Li_2TiO_3) and lithium silicates (Li_2SiO_3, Li_4SiO_4), and CO_2. Absorption characteristics were evaluated by observing weight change of absorbents using thermogravimetric analysis (TGA). Weight increase indicates CO_2 absorption. Among all these candidates in Table 1, another reversible reaction of lithium orthosilicate (Li_4SiO_4) was confirmed (Eq.2). As shown in Fig. 1, the reaction rate of Eq. 2 is much faster than that of Eq.1. Since lithium orthosilicate is synthesized from inexpensive silica and lithium carbonate, we believe this is the most promising material to use at large scale CO_2 separation system.

$$Li_4SiO_4 + CO_2 = Li_2SiO_3 + Li_2CO_3 \qquad \text{Eq.2}$$

By fabricating porous body of these absorbents, lithium oxide in absorbents reacts with CO_2 and produces molten lithium carbonate. The molten lithium carbonate is stored in micro-pores of the porous body by capillary force. When temperature is increased above 700^oC, lithium carbonate decomposes by reverse reaction and returns to an original state releasing CO_2. Figure 2 shows a typical TGA reproducibility of lithium orthosilicate in pure CO_2 atmosphere. Since equilibrium temperature of Eq. 2 is approximately 700ºC, 850ºC is very sufficient temperature to achieve complete CO_2 emission in this atmosphere. As you can see, clear cycles of weight change were observed corresponding to these temperature swings. The width of weight change after 5 cycles almost equal to that of initial change.

Table 1　Lithium-containing oxides tested in this study.

Absorbent	Formula Weight	Density (g/cm^3)	Oxide	Equilibrium Temp.
Li_2ZrO_3	153.1	3.6	ZrO_2	715ºC
$2LiFeO_2$	189.6	4.4	Fe_2O_3	510ºC
$2LiNiO_2$	195.3	4.8	Ni_2O_3	No data
$2LiAlO_2$	131.8	3.4	Al_2O_3	348ºC
Li_2TiO_3	109.8	3.5	TiO_2	315ºC
Li_2SiO_3	90.0	2.5	SiO_2	260ºC
Li_4SiO_4	119.8	2.4	Li_2SiO_3	720ºC

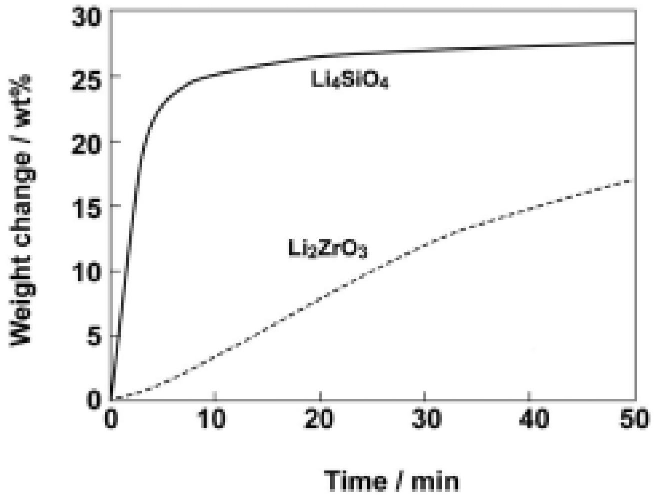

Figure 1　TGA results of lithium orthosilicate and lithium zirconate during heating at 500^{o}C in 20% CO_2 (Ambient pressure).

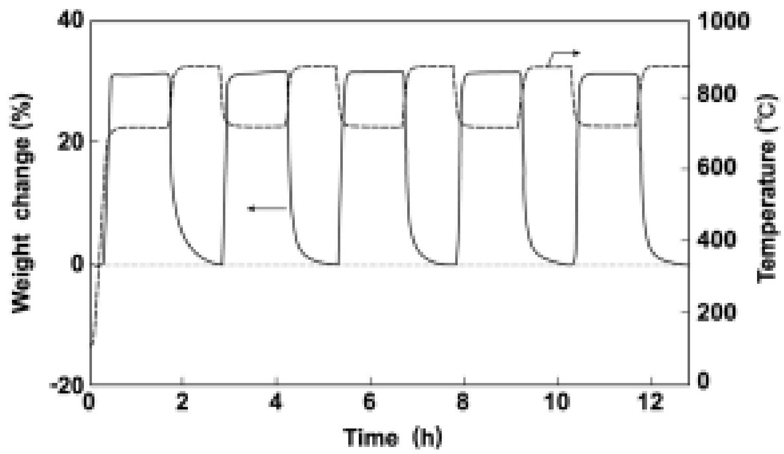

Figure 2　TGA reproducibility of lithium orthosilicate during heating at 700^{o}C and 850^{o}C in pure CO_2 (Ambient pressure).

4. Application

Lithium orthosilicate will be a compact absorbent. Absorption capacity of 400 times in volume ratio was already confirmed experimentally. Small reaction heat of lithium orthosilicate is another advantage. All regenable absorbents require endothermic reaction heat during regeneration process of the absorbent. It is generally believed that the small value of reaction heat is beneficial to reduce energy penalty of CO_2 separation. Our experimental data indicates that Eq. 2 has reaction heat of *ca*.70 kJ/mol above 450ºC. This value is smaller than that of amine and suggests concrete reduction of energy penalty. Table 2 summarized comparison of lithium orthosilicate with zeolite adsorbent and amine absorbent. It is noteworthy that there is no other material operable at high temperature beyond 400ºC. We believe these advantages make every CO_2 separation system compact and energy efficient.

Application in power plants as a global warming countermeasure is a prospective plan. In integrated gasification combined cycle (IGCC), temperature of fuel gas, *i.e.*, around 500^{o}C, is preferable for the absorption of this absorbent, as shown in Fig. 3. For continuous separation, a system with two reaction vessels which contain absorbent is proposed. In order to minimize energy penalty of CO_2 separation, we now focus on Absorption Enhanced Reforming (AER) system. Figure 4 shows basic idea of the plan. Combining this absorbent with steam reforming, we can expect higher reaction yield of hydrogen, because of equilibrium shifting. Main point of this plan is the heat exchange between absorbent and catalyst. Absorbents can supply about half of endothermic reaction heat of steam reforming. This part of study is supported by Japanese government founded organization; New Energy and Industrial Technology Development Organization (NEDO).

5. Summary

We found novel absorbents operable at high temperature. In particular, lithium orthosilicate is thought to be a promising material to design new CO_2 separation systems on the basis of its large absorption capacity, small reaction heat and inexpensive raw materials. Our current research effort is focused on Absorption Enhanced Reforming (AER) system, in which we are expecting chemical equilibrium shifting and recovery of exothermic heat of absorption. This is a work with New Energy and Industrial Technology Development Organization (NEDO) .

Table 2 Comparison with other technologies.

	Operable temperature	CO_2 capacity (volume ratio)	Selectivity (for N_2, H_2)
This absorbent	RT—700℃	400—500	Very good
Physical adsorbent (Zeolite)	RT	70—80	good
Chemical absorbent (Amine)	RT	20—30	Very good

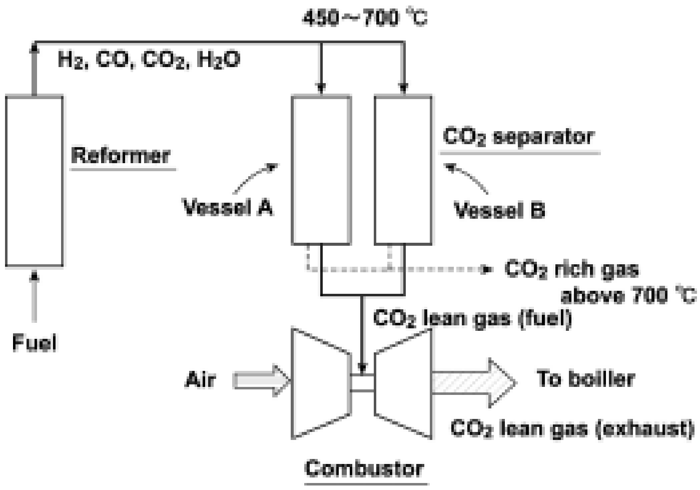

Figure 3 Example of CO_2 capturing at power plants.

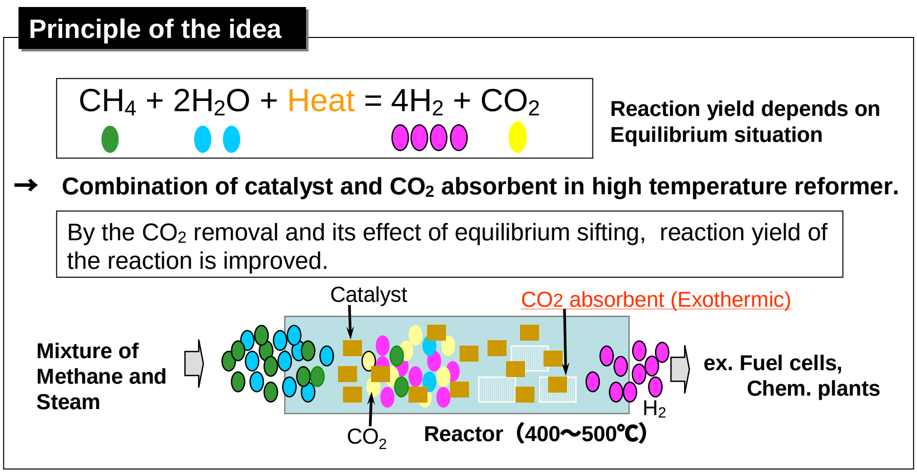

Figure 4 Idea for Absorption Enhanced Reforming (Schematic figure)

References

- K. Nakagawa and T. Ohashi, *J. Electrochem. Soc.*, **145**, 1344 (1998).
- K. Nakagawa and T. Ohashi, *Electrochemistry*, **67**, 618 (1999).
- M. Kato, K. Nakagawa and K. Essaki, *J. Ceramics Soc. Jpn.*, **109**, 911 (2001).
- M. Kato, S. Yoshikawa and K. Nakagawa, *J. Material Science Letters*, **21**, 485 (2002).