Carbonation/Decarbonation of Ca-Solid Reactant Derived from Natural Limestone for Thermal-Energy Storage and Temperature Upgrade

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The carbonation and decarbonation of the Ca solid reactant prepared by the natural limestone powder were analyzed about the effect of annealing temperature on the reactivity and the durability in repetitive operation. The solid reactants annealed at 1073 K and lower had the larger reproducible pore volume in the range from 10 to 25 nm, and showed the higher conversion of carbonation. The solid reactants annealed at 1273 K indicated the excellent durability of repetitive cyclic procedure, which was comparable to that of the reactant prepared by the metal alkoxide method.

Introduction

From the viewpoint of energy utilization and global environmental protection, the effective heat energy management must be introduced. Thermal energy storage and temperature upgrade is one of the key technologies for the efficient operation of all the system using heat energy. Chemical heat pumps (CHPs) are one of the most attractive thermal energy storage and upgrade technologies. Some researchers proposed a CHP usable even in the high temperature range using decarbonation of calcium carbonate and carbonation of calcium oxide:

\[
\text{Carbonation: } \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad (1)
\]

\[
\text{Decarbonation: } \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (2)
\]

This CHP system has the advantage that the energy storage density is very high (about 3.26 GJ/m³), the reaction products are free from toxicity and corrosiveness, and the CaCO₃ raw material is abundantly available. Barker (1973, 1974) reported that the surface area of the reaction solid decreases as a result of the growth of primary particles of calcium carbonate and that reversibility deteriorates when reactions (1) and (2) are reversibly carried out under high pressure. Recently CaO as regenerable CO₂ sorbents in industrial processes, using the carbonation/decarbonation cycle of CaO/CaCO₃ at high temperature, has attracted increased attention for mitigation of greenhouse gas emissions (Abanades et al., 2003, 2004). Although the mechanism of gas–solid reaction using limestone as raw material has been investigated in detail for a long time, there are few reports on enhancing the reversibility of these reactions (Gupta et al., 2002). The gas–solid system CHPs using CaO or Ca-solid reactants has been vigorously continued to research and develop in Japan. Kato et al. (1996, 1997, 1999) researched and proposed the gas–solid system CHPs using CaO, MgO or PbO solid reactants. Ogura et al. (2002, 2003, 2004; Fujimoto 2002a, 2002b) reported the application using Ca-solid reactant and the applicability of a scallop to CHP.

Aihara et al. (1990) succeeded in improving the reversibility of the reaction solid for the thermochemical hydrogen production process by using a metal alkoxide method in the preparation stage. The reaction solid by this method maintained the cyclic reaction reversibility by forming an inert framework of complex oxide to retain the reactant with its changing volume and the void that buffers this volume change simultaneously. Aihara et al. (2001) regarded the reaction solid showing the stable cyclic reaction of calcium oxide and calcium bromide as being applicable for that of calcium oxide and calcium carbonate as well, and also succeeded in stable cyclic operations of carbonation and decarbonation for this CHP system.
In order to develop and improve the reaction solid, a numerical analysis model based on the change in micro-order pore structure between the constituent particles (Nagura and Aihara, 2001; Kobayashi et al., 2002), and nano-order pore structure in the particles (Aihara et al., 2004) was proposed and analyzed the carbonation and decarbonation of this Ca solid reactant prepared by using CaCO3 reagent as raw material.

In this study, the carbonation and decarbonation of the Ca solid reactant derived from natural limestone was analyzed about the effect of annealing temperature on the reactivity and the durability in the repetitive operation, and discussed on the basis of the observed data and the pore structure change model.

1. Experimental

1.1 Preparation of reaction solid by thermal decomposition of powdered calcium carbonate

Solid reactants were prepared by thermal decomposition of two types of raw material powders, which were calcium carbonate reagent (assay 99%, Junsei Chemical Co., Ltd.) with an average particle size of 5 µm and natural limestone finely powdered (assay 98.5%, Takehara Kagaku Kogyo Co., Ltd.) with an average particle size of 2.7 µm. Each calcium carbonate powders were dispersed in ethanol, filtered with suction, formed into spherical pellets of 4 mm in diameter, and dried at 383 K for 24 h before annealing. The solid reactants were annealed at the desired temperatures of 923 to 1273 K for 3 h. All reaction solids were kept at 773 K until just before reaction experiments to prevent reactions with moisture, etc.

1.2 Experimental apparatus

The experimental apparatus is shown in Figure 1. A reactor (quartz glass tube; height, 500 mm; inside diameter, 25 mm) was fixed in an electric furnace kept at a constant temperature by a controller. The solid reactant placed in a platinum basket was suspended with platinum wires from a balance. A gas mixture of carbon dioxide and dry nitrogen as the carbonation gas, or dry nitrogen as the decarbonation gas, was injected into the reactor.

1.3 Analysis of the structure of the solid reactant

The structures of solid reactants were examined using a scanning electron microscope (JSM-6301F, JEOL Ltd.), and a nitrogen absorption-desorption analyzer (OMNISORP 100CX, Beckman Coulter, Inc.).

2. Results and Discussion

2.1 Conversion profiles and structure changes between carbonation and decarbonation

Figure 2 shows the conversion profiles of solid reactant derived from natural limestone for one cyclic procedure of carbonation and decarbonation. Each reaction was operated at 923 K. The feeding gases for carbonation and decarbonation were 100% carbon dioxide and 100% dry nitrogen, respectively.

The conversion, X, is defined as follows:

\[ X = \frac{N_{\text{CaO}}}{N_{\text{CaCO}_3}} \]

while \( N_{\text{CaO}}^0 \) is the initial concentration of calcium oxide [mol/m³] and \( N_{\text{CaCO}_3} \) is the concentration of calcium carbonate [mol/m³] estimated from the change of weight at reaction time.

Figure 3 shows the effect of annealing temperature on the conversion of carbonation. The conversion of carbonation increased with the drop in the annealing temperature of 1273 to 1073 K and stopped increasing below 973 K. Figures 4 and 5 indicate the BET specific surface areas and the pore size distributions of the each solid reactant before the first carbonation.
As the annealing temperature became higher, the specific pore volume and the specific surface area decreased with sintering. The pore volume change with plugging the pores and decreasing the surface area in the solid reactant during carbonation and decarbonation were thought to occur the drops of the reactivity of carbonation.

2.2 SEM analysis

Figures 6(a) and 6(b) show SEM photographs of solid reactants after annealing at 1023 K and 1273 K, respectively. It was observed that sintering of CaO particles proceeded further at the higher annealing temperature in Figure 6(b). It was thought that this fusion between CaO particles caused to reduce the specific surface area and the pore volume of solid reactant.

2.3 Conversion profiles and pore structure change under cyclic operation

The conversion profile of the solid reactant at the annealing temperature of 1273 K for cyclic procedure was shown in Figure 7. Each conversion after carbonation of this solid reactant was stable for 4 cycles, which was comparable to that of the reactant prepared by the method proposed by our group (Aihara et al., 2001). The same cyclic procedure of carbonation and decarbonation was carried out for each solid reactant at the different annealing temperatures. The comparison of conversions after carbonation of these solid reactants is shown in Figure 8. Compared with the conversion for the reactant annealed at 1273 K, those for the other reactants annealed at the lower temperatures were higher but decreasing with the cyclic numbers. There was less difference of the profiles at the lower
temperatures than 1073 K.

Figure 9 shows the comparison between the 4 cycle conversion profiles of solid reactant prepared using the natural limestone powder and the CaCO$_3$ chemical reagent. Though these solid reactants were annealed at the same temperature of 1273 K, the durability in the cyclic repetition for the reactant derived from the natural limestone was more excellent than that derived from the CaCO$_3$ reagent. Using the reactant derived from the CaCO$_3$ reagent, the sintering between mutual particles was thought to make the change of pore structure and to decrease the reactivity. The addition of the inert material in the solid reactant suppresses mutually sintering and is effective in the improvement of the stable reversibility of the cyclic reaction (Aihara et al., 2001).

The natural limestone contained MgCO$_3$ 1%, SiO$_2$ 0.2%, Al$_2$O$_3$ 0.1% as impurities. It was thought that these impurities played a role of the inert material for the cyclic reaction. Figure 10 shows SEM photographs of the surface of the reactants annealed at 1073 and 1273 K before and after the repetitive operation. The apparent big structural change observed in the case of the reactant derived from CaCO$_3$ reagent (Aihara et al., 2001) weren’t found in these reactants. The slight change found in the case after the 1st cycle annealed at 1073 K was considered to affect the gradual drop in the conversion under the repetitive operation which was found in Figure 8.

Though the drops in the conversion occurred in the reactant annealed at the lower temperatures, the values of conversion were higher than those annealed at the higher temperatures. The reason was thought as follows. Figures 11(a), (b) and (c) show the pore size distributions of the reactants derived from the natural limestone annealed at 1273 K and 1073 K and from the CaCO$_3$ reagent annealed at 1273 K, respectively. The pore size distributions and the total pore volumes of limestone and CaCO$_3$ annealed at 1273 K showed similar results in Figures 11(a) and (c). Though most of the pore volume disappeared before carbonation (cycle #0), after the first cycle (cycle #1) the pore volume from 10 to 25 nm was reproduced and repeated disappearance and appearance. This disappearance of
the pore volume from 10 to 25 nm was observed in the reactant at the higher annealing temperature than 1173 K. On the other hand, the fair amount of pore volume from 15 to 25 nm of the limestone annealed at 1073 K remained without disappearing before the 1st cycle and larger volume of the pore in this range was continued to reproduce after the 1st cycle. Because the volume of the reproducible pore corresponds to the amount of carbonation by absorbing CO₂, the difference of these pore volume occurred the difference of the durability performance between the reactants at the different annealing temperatures.

**Conclusion**

The carbonation and decarbonation of the Ca solid reactant derived from natural limestone were analyzed about the effect of annealing temperature on the reactivity and the durability in repetitive operation. The solid reactants annealed at 1073 K and lower had the larger reproducible pore volume in the range from 10 to 25 nm, and showed the higher conversion of carbonation. The solid reactants annealed at 1273 K indicated the excellent durability of cyclic procedure comparable to that of the reactant prepared by the alkoxide method.

**Literature Cited**


