Particle size dependence of CO₂ absorption rate of powdered Li₄SiO₄ with different particle size

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Particle size dependence of CO₂ absorption rate of powdered Li₄SiO₄ with four kinds of particle sizes was studied by SEM observation, particle size distribution measurement, and thermogravimetry. Average particle sizes of the powdered single phase Li₄SiO₄ samples were estimated about 26 μm, 34 μm, 53 μm, 70 μm, respectively by the particle size distribution measurement and SEM observation. The measurement of apparent rate constant k for the CO₂ absorption reaction showed that k values of all the powdered Li₄SiO₄ samples increase with the increasing measurement temperature T , following the Arrhenius equation in the region of 620–660°C, while the k values abruptly increase deviating the Arrhenius equation over 670°C. It was also noted that the k values seem to depend on the particle size of the powdered Li₄SiO₄ samples, that is, the k values increase with the decreasing particle size. Moreover, difference between the k values of all the powdered samples at same temperature was found small in the region of 620–660°C, while the difference was found large over 670°C. For Li₄SiO₄ with smaller particle size, $\Delta k = k_{700^\circ\text{C}} - k_{660^\circ\text{C}}$ was found larger, vice versa, the Δk was found smaller for Li₄SiO₄ with larger particle size. The values seem to correspond with reaction mechanism for CO₂ absorption of Li₄SiO₄ particle.

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1. Introduction

It is well-known that Global Warming is quite a large problem in the world. It must be a very important and urgent challenge to solve the problem as soon as possible. This sense of urgency has been shown by the coming into effect of the Kyoto Protocol. It is thought that one of the main causes of the Global Warming is carbon dioxide CO₂ produced as one of the exhaust gases from power plants generating electricity and from other factories. Thus, it is desired to reduce the amount of the produced CO₂ gas.

However, it is difficult to reduce the amount of the CO₂ gas because it is more difficult to reduce the amount of electricity generated at present, and rather, more generation of electricity appears to be necessary for progress in developing countries. Therefore, it is important to separate CO₂ in the exhaust gases from power plant as well as the reducing the amount of produced CO₂. Therefore, effective CO₂ separation techniques or systems are desired.

Many previous superior studies^{1)–12)} have already reported on the separation techniques and systems. Researchers of Toshiba Corporation have developed a novel separation technique that employs a chemical reaction of lithium-containing oxides, such as Li₂ZrO₃ and Li₄SiO₄, with CO₂.^{5)–12)} According to these reports,^{5)–12)} it has been thought that Li₄SiO₄ is a very efficient CO₂ absorbent because 1 g of Li₄SiO₄ can absorb 0.367 g of CO₂, and the absorption is supposed to depend on the following reaction (1).¹¹⁾

On the basis of the reaction, CO₂ reacts with Li₂O component

of Li₄SiO₄ and changes to solid Li₂CO₃ when CO₂ is absorbed in Li₄SiO₄, and the maximum CO₂ absorption

$\left(\frac{1 \times (\text{molecular weight of CO}_2)}{1 \times (\text{molecular weight of Li}_4\text{SiO}_4)} \times 100\% \right)$ is theoretically esti-

mated as 36.7 mass%, if the reaction completes. Experimental value¹¹⁾ of the maximum CO₂ absorption is consistent with 36.7 mass% of the estimated one at 700°C. Moreover, it has been confirmed that the reaction (1) is reversible, that is, the reaction (1) progresses toward the right direction (→) below 700°C, and the left direction (←) over 700°C. This result means that Li₄SiO₄ can be repeatedly used as a novel CO₂ absorbent. However, these results mentioned were measured on the basis of thermodynamics, not on the rate theory. Therefore, results of the CO₂ absorption on the basis of the rate theory must be desirable. From a view point of the absorption rate for Li₄SiO₄, Essaki et al. have studied on time dependence of the CO₂ absorption reaction at a constant temperature for Li₄SiO₄.¹³⁾ In the report, weight increase (CO₂ absorption) of Li₄SiO₄ was measured with time, and temperature dependence of the absorption rate was discussed, however, rate constant k and reaction order n were not measured.

Recently, we measured apparent rate constant k of the CO₂ adsorption for two kinds of powdered Li₄SiO₄ with small particle size and large particle size by thermogravimetry using very fast heating method and studied temperature dependence of the apparent rate constant k in the temperature region of 620–700°C, and confirmed that the k values increases with the increasing measurement temperature T , following the Arrhenius equation in the region of 620–660°C, while the k values deviate from the Arrhenius equation over 670°C, that is, the k values abruptly increases over 670°C.¹⁴⁾ In addition, in the study, particle size dependence of the rate constant k for the powdered Li₄SiO₄ was

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briefly studied and discussed, but it was not enough.

Therefore, in this paper, we study particle size dependence of the rate constant k of the powdered Li₄SiO₄ with four kinds of particle sizes by means of XRD, SEM observation, particle size distribution measurement, and thermogravimetry, and discuss mechanism of the CO₂ absorption for the powdered Li₄SiO₄.

2. Experimental procedures

2.1 Sample preparation

Li₄SiO₄ ceramics samples were prepared by the solid state method using Li₂CO₃ powder reagent (99.999% purity, Rare Metallic Co., Ltd.), and SiO₂ powder reagent (99.99% purity, Rare Metallic Co., Ltd.). Before these reagents were weighed for the preparation, thermogravimetry using a thermogravimetric instrument (ULVAC-RIKO thermobalance type 9600) was performed on these reagents in order to examine whether absorption moisture was contained or not in these reagents. After the thermogravimetry, these reagents were weighed in an appropriate molar ratio and mixed/ground in a sardonyx mortar by hand for 1 h. Obtained powder mixtures were pressed into a pellet, and the pellet was sintered on a gold plate at 700, 800, 900, and 1000°C for 20 h in air. Particle size of obtained Li₄SiO₄ ceramics was controlled by these sintering temperatures. By this procedure, Li₄SiO₄ ceramics samples with four kinds of particle sizes were obtained. The obtained ceramics samples were examined by XRD to confirm whether the Li₄SiO₄ samples were single phase or not.

2.2 Particle size measurement

SEM observation was performed on both Li₄SiO₄ ceramics samples and powdered Li₄SiO₄ samples in order to observe the particle size of all the samples. Moreover, median (50%) particle

size of the powdered Li₄SiO₄ samples was measured thorough particle size distribution (frequency distribution and accumulative distribution) by laser diffraction and scattering method using LASER MICRON SIZER LMS-30 (SEISHIN ENTERPRISE Co., Ltd.). In this measurement, methanol was used as the solvent because Li₄SiO₄ is soluble in water.

2.3 CO₂ absorption measurement

For measurement of the CO₂ absorption for Li₄SiO₄, four kinds of powdered Li₄SiO₄ samples were prepared by the procedure, in which the four kinds of ceramics Li₄SiO₄ samples with different particle sizes were quite carefully ground in a sardonyx mortar in order to remain the particle sizes in the ceramics samples.

The CO₂ absorption measurement was performed on these four powdered Li₄SiO₄ samples. For the measurement, 20 mg of the powdered Li₄SiO₄ samples was used, respectively. The powdered Li₄SiO₄ sample was put in an alumina cell. The alumina cell was set in the thermogravimetric instrument, where pure CO₂ gas was flowing with 150 mL of the flowing rate during the measurement. Thus, CO₂ gas was sufficiently provided to the powdered Li₄SiO₄ sample during the measurement. Nine kinds of measurement temperatures were chosen as 620, 630, 640, 650, 660, 670, 680, 690, 700°C. Weight change (TG) and DTA of the powdered Li₄SiO₄ samples were, in-situ, measured when the sample was quickly heated with about 400°C/min. to a target measurement temperature and was kept at the temperature in the CO₂ atmosphere until the measurement was finished. Temperature of the sample was directly measured by a thermo couple. The CO₂ flowing rate and the measurement temperatures were decided according to our previous report.¹⁴⁾

Fig. 1. SEM photographs of the Li₄SiO₄ ceramics samples and powdered samples, (A) sample sintered at 700°C, (B) sample sintered at 800°C, (C) sample sintered at 900°C, (D) sample sintered at 1000°C, and (a) powdered sample from the Li₄SiO₄ sintered at 700°C, (b) powdered sample from the Li₄SiO₄ sintered at 800°C, (c) powdered sample from the Li₄SiO₄ sintered at 900°C, (d) powdered sample from the Li₄SiO₄ sintered at 1000°C.

2.4 Rate analysis for the CO₂ absorption

Apparent rate constant k of the CO₂ absorption for the powdered Li₄SiO₄ samples was estimated by the rate theory. Since we supposed that the CO₂ absorption reaction is a pseudo first order reaction in our previous report,¹⁴⁾ the first order reaction equation was applied for the estimation in this study although some kinds of rate equations have been known.^{15)–17)} The first order reaction equation used is shown below,

$$-\frac{d[\text{Li}_4\text{SiO}_4]}{dt} = k[\text{Li}_4\text{SiO}_4]_t P_{\text{CO}_2} \quad (2)$$

$$\ln\left(\frac{[\text{Li}_4\text{SiO}_4]_0}{[\text{Li}_4\text{SiO}_4]_t}\right) = kP_{\text{CO}_2}t \quad (3)$$

$$\ln\left(\frac{a}{a-x}\right) = kP_{\text{CO}_2}t \quad (4)$$

where, k is the apparent rate constant, and $[\text{Li}_4\text{SiO}_4]_0$ and a are the initial amount of the powdered Li₄SiO₄ samples used in the measurement, and $[\text{Li}_4\text{SiO}_4]_t$ and $(a-x)$ are the residual amount of the powdered Li₄SiO₄ samples at a reaction time t . P_{CO_2} is the pressure of CO₂ gas used as atmosphere for the measurement. In this measurement, P_{CO_2} was fixed as 0.1 MPa. The amount of x was calculated from weight change (weight increase) at a time t and at a measurement temperature T for the powdered Li₄SiO₄ samples in the measurement. We used the Eq. (4) for the actual estimation. Details of the estimation have been described in our

previous report.¹⁴⁾

3. Result and discussion

3.1 Sample preparation

XRD measurement showed that four kinds of Li₄SiO₄ ceramics samples sintered at 700, 800, 900, 1000°C for 20 h in air were single phase. SEM photographs of the four ceramics samples are shown in Figs. 1(A)–(D). From Fig. 1, it is found that particle size of the ceramics samples are different each other, that is, the particle size of the samples sintered at higher temperature is larger than that of samples sintered at lower temperature. Thus, we could obtain four kinds of Li₄SiO₄ ceramics samples with different particle size.

3.2 Particle size measurement

For the CO₂ absorption measurement, four kinds of powdered Li₄SiO₄ samples were prepared from the Li₄SiO₄ ceramics samples by the procedures mentioned under the experimental part. SEM photographs of the four powdered samples are shown in Figs. 1(a)–(d). From the figure, particle sizes of the powdered samples look mutually different. In order to measure average particle size of the powdered samples, particle size distribution measurement was performed on the powdered samples. Measured frequency distribution and accumulative distribution of the powdered samples are shown in Figs. 2(a)–(d). From the figure, it is recognized that the frequency distributions of the samples look almost symmetry. Median particle sizes of the samples were measured about 26 μm for the powdered sample (700°C), 34 μm

Fig. 2. Accumulative and frequency distributions of the powdered samples, (a), (b), (c), (d) shown in Fig. 2.

for the powdered sample (800°C), 53 μm for the powdered sample (900°C), and 70 μm for the powdered sample (1000°C), respectively. Because the frequency distributions look almost symmetry, the median particle size would be equated with average particle size. In addition, it was difficult to measure the median particle size of the powdered sample (700°C) which easily agglomerates due to the smaller particle size.

3.3 CO₂ absorption measurement

Weight change (weight increase) of the powdered Li₄SiO₄ samples was measured with reaction time t at a target reaction temperature T by the thermogravimetric instrument mentioned under the experimental part, and then reaction rate constant k was estimated. As a typical example of the estimation, $\ln\left(\frac{a}{a-x}\right)$ was plotted to the reaction time t at 700°C for the samples with 26 μm , 34 μm , 53 μm , and 70 μm of the particle sizes in Fig. 3. According to the first order reaction Eq. (4), increase of $\ln\left(\frac{a}{a-x}\right)$ corresponds with progression of the CO₂ absorption reaction. From Fig. 3, it is found for the powdered samples with smaller particle size that $\ln\left(\frac{a}{a-x}\right)$ rises in shorter reaction time, that is, the CO₂ absorption reaction seems to progress in shorter reaction time. It is noted that, first, $\ln\left(\frac{a}{a-x}\right)$ linearly increases with a constant slope, then the slope decreases. Thus, a break point is found in the data of $\ln\left(\frac{a}{a-x}\right)$ to time. The break point means that progression of the CO₂ absorption reaction seems to be disturbed by some kind of factor. According to previous reports,^{11),13),14)} the reason why the break point is found that the progression of the CO₂ absorption reaction could be disturbed by Li₂CO₃ and Li₂SiO₃ phases which are formed on Li₄SiO₄ particle when the reaction between Li₄SiO₄ and CO₂ gas proceeds. Therefore, the more the CO₂ absorption reaction proceeds, the more difficult for the reaction to proceed due to the Li₂CO₃ and Li₂SiO₃ phases.

On the other hand, a tendency is found that the slopes decrease with the increasing particle size. On the basis of the equation (4), the slope corresponds with kP_{CO_2} , and P_{CO_2} was fixed as 0.1 MPa in the measurement. According to our previous report,¹⁴⁾ in this study, we also supposed that the CO₂ absorption reaction is a

Fig. 3. Reaction rate analysis on the CO₂ absorption reaction at 700°C by the first order reaction equation for all the powdered samples (a), (b), (c), (d) shown in Fig. 2.

pseudo first order reaction until the time which the break point is found at. Thus, apparent rate constant k for all the samples was estimated from the measured slope ($kP_{\text{CO}_2} = k \times 0.1$) at 620, 630, 640, 650, 660, 670, 680, 690, 700°C. Temperature dependence of the estimated k values for all the samples is shown in Fig. 4. In Fig. 4, a tendency is found for all the samples that the k values gradually increase with the increasing reaction temperature in the region of 620–660°C, but the k values abruptly increase over 670°C. It should be noted that degree of the abrupt increase of the k values is the largest for the case of the sample with the smallest average particle size (26 μm).

The Arrhenius plot was performed on the data of k and T for all the samples, following the Arrhenius equation shown below. Results are shown in Fig. 5. From Fig. 5, the reaction

$$\ln k = \ln A - \frac{E_a}{RT}$$

mechanism seems to change around 670°C because the $\ln k$ values abruptly increase around 670°C. In our previous report,¹⁴⁾ we discussed that the change in the k (or $\ln k$) values seems to depend

Fig. 4. Temperature dependence of the apparent rate constant k for all the powdered samples.

Fig. 5. Arrhenius plot for the apparent rate constant k and temperature T for all the powdered samples.

on a change of the surface condition (or state) of Li_4SiO_4 particle due to the instability (or melting) of Li_2CO_3 phase on the surface of the Li_4SiO_4 particle because, as previously mentioned, the Li_2CO_3 and Li_2SiO_3 phases formed with progression of the CO_2 absorption reaction can disturb further progression of the CO_2 absorption reaction of Li_4SiO_4 . Therefore, it seems that the k values could abruptly increase due to the melting or breaking of the Li_2CO_3 phase, that is, CO_2 gas could furthermore attack the surface of Li_4SiO_4 particle.

Since the k values abruptly increase over 670°C , two kinds of activation energies were estimated from the slopes in two regions of $620\text{--}660^\circ\text{C}$ and $680\text{--}700^\circ\text{C}$. From the estimation, it seems that all the samples have almost same activation energies about 114 kJ mol^{-1} in the region of $620\text{--}660^\circ\text{C}$, and 55 kJ mol^{-1} in the region of $680\text{--}700^\circ\text{C}$, that is, there is almost no large difference between the activation energies for all the samples. The results would mean that, roughly, all the samples seem to have almost same CO_2 absorption mechanism. However, we can not more precisely consider on the CO_2 absorption mechanism by the activation energies because the logarithm term ($\ln k$) makes us illegible on more precise consideration.

On the other hand, it was found that the k values seem to depend on the particle size of the powdered Li_4SiO_4 samples. Here, degree of abrupt increase in the k values over 670°C is considered to the particle size. $\Delta k = k_{700^\circ\text{C}} - k_{660^\circ\text{C}}$ was calculated as the degree of the abrupt increase in the k values over 670°C . In Fig. 6, Δk values were plotted to half of the particle size which would mean a distance between the surface and the centre of the Li_4SiO_4 particle. From Fig. 6, it is found that the Δk values gradually decrease in the region of $10\text{--}18\text{ }\mu\text{m}$, and abruptly decrease in the region of $20\text{--}25\text{ }\mu\text{m}$, then gradually decrease in the region of $26\text{--}35\text{ }\mu\text{m}$ when the half of the particle size increases. The results mean that surface reaction process would be the rate controlling factor for the CO_2 absorption reaction of Li_4SiO_4 in the case of the larger Δk value, while diffusion process is the rate controlling factor in the case of the smaller Δk value. Thus, considering that the large Δk value for Li_4SiO_4 with smaller particle size could be caused by a change in surface state of the Li_4SiO_4 particle, at the same time, diffusion distance for CO_2 from the surface to the centre of Li_4SiO_4 particle is longer for Li_4SiO_4 with larger particle size, the Δk value could be an impor-

tant factor to show which process is the rate controlling one in the CO_2 absorption mechanism of Li_4SiO_4 . Advanced researches must be necessary on both the surface and diffusion processes by another reaction rate equations or methods^{15)–18)} in the future.

4. Conclusion

We studied on particle size dependence of CO_2 absorption rate of the powdered Li_4SiO_4 with four kinds of particle sizes by XRD, SEM, and thermogravimetry. Four kinds of the powdered Li_4SiO_4 samples were prepared from four kinds of Li_4SiO_4 ceramics sintered at 700 , 800 , 900 , and 1000°C in air by the solid state method using Li_2CO_3 and SiO_2 . From the results of XRD, it was confirmed that the sintered Li_4SiO_4 can be obtained as single phase at all the sintering temperatures. From the particle size distribution measurement and SEM observation, average particle sizes of the powdered (single phase) Li_4SiO_4 samples were estimated about $26\text{ }\mu\text{m}$, $34\text{ }\mu\text{m}$, $53\text{ }\mu\text{m}$, $70\text{ }\mu\text{m}$, respectively. From the measurement of apparent rate constant k for CO_2 absorption of the powdered Li_4SiO_4 , it was found that the k values increases with the increasing measurement temperature, following the Arrhenius equation in the region of $620\text{--}660^\circ\text{C}$, however, the k values abruptly increases over 670°C for all the powdered Li_4SiO_4 samples. On the other hand, the k values seems to depend on the particle size of the powdered samples, that is, the k values increases with the decreasing particle size. Difference between the k values of the four kinds of the powdered samples was found small in the region of $620\text{--}660^\circ\text{C}$, while the difference was found large over 670°C . Degree of the abrupt increase in the k values over 670°C ($\Delta k = k_{700^\circ\text{C}} - k_{660^\circ\text{C}}$) abruptly changes around $20\text{ }\mu\text{m}$ as the half of the particle size. Considering that the large Δk value for Li_4SiO_4 with smaller particle size could be caused by a change in surface state of the Li_4SiO_4 particle, at the same time, diffusion distance for CO_2 from the surface to the centre of Li_4SiO_4 particle is longer for Li_4SiO_4 with larger particle size, the Δk value could be an important factor to show which process is the rate controlling one in the CO_2 absorption mechanism of Li_4SiO_4 .

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Fig. 6. Relation between the degree of the abrupt increase in the k values and the half of the particle size for all the samples. The degree of the abrupt increase in the k values was defined as $\Delta k = k_{700^\circ\text{C}} - k_{660^\circ\text{C}}$.

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