Supporting Information

Effect of lithium-compound addition on the dehydration and hydration of calcium hydroxide as a chemical heat storage material

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Figure S1 shows a DTG curve obtained by differentiating with temperature the weight change when the sample was heated from room temperature to 600 °C. The temperature showing the minimum value in the DTG curve was defined as the dehydration peak temperature. The dehydration peak temperature is the temperature at which the dehydration reaction rate is maximized when the sample is heated at a constant heating rate. A decrease in the dehydration peak temperature means that the dehydration reaction of calcium hydroxide proceeds at a lower temperature.
Figure S1. DTG curve heated to 600 °C: (a) Ca(OH)$_2$-w, (b) LO10, (c) LC10, (d) LCO10 (e) LO5LC5, (f) LO10LCO5, (g) LC10LCO5.
Table 2 shows the reaction rate constant of the dehydration reaction of calcium hydroxide at 350 °C and the R-square value between the measured and calculated values.

First, we assumed that the molar fraction of 0.9–0.4 corresponds to a zero order reaction. The mole fraction of the calculated value is represented by Eq. (2). Using the least-squares method, the reaction rate constant, \( k_0 \), that minimizes the error between the measured and calculated values was determined. Now, we assumed that the molar fraction of 0.3–0.1 corresponds to the first order reaction. The mole fraction of the calculated value is represented by Eq. (3). Similarly, the least-squares method was determined to find the reaction rate constant, \( k_1 \), that minimizes the error between the measured and calculated values. The molar fraction of 0.9–0.4 was used for the zero-order reaction was because the error between the predicted value and the actual measurement value was small. When the zero-order reaction was calculated from 0.3, 0.4, and 0.5, successively, the error between the calculated value and the actually measured value was the smallest when the molar fraction of 0.9–0.4 was adopted for the zero-order reaction. Also, when model fitting was performed on the assumption that all dehydration reactions were zero-order reactions or first-order reactions, there was a large error between the measured values and calculated values (Figure S2).
Figure S2. Measured and calculated mole fraction of Ca(OH)$_2$ for Ca(OH)$_2$-w at 350 °C; (a) calculated as zero-order reaction, (b) calculated as first-order reaction, (c) calculated as a two-step reaction (0.4<x<0.9: zero-order reaction, 0.1<x<0.3: first-order reaction).
Using the calculated rate constant, the change in molar fraction in the calcium hydroxide dehydration test was calculated and compared with the measured value. Between the zero-order reaction and the first-order reaction (mole fraction range \(x = 0.4–0.3\)), the value was calculated by taking the weighted average of the two values obtained by assuming a zero-order and a first-order reaction. The coefficient of determination \(R^2\) representing the magnitude of variance between the measured value and the calculated value was determined using Eq. (S1). The closer the \(R^2\) value is to 1, the smaller is the difference between the measured and calculated values.

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R^2 = 1 - \frac{\sum_{i=1}^{n}(x_i - \hat{x}_i)^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}
\]  

(S1)

\(R^2\) is the coefficient of determination, \(x_i\) is the measured value, \(\hat{x}_i\) is the calculated value, and \(\bar{x}\) is the average of the measured values. **Figure S3** shows the measured and calculated mole fractions of Ca(OH)\(_2\).
Figure S3. Measured and calculated mole fraction of Ca(OH)$_2$ for samples at 350 °C; (a) Ca(OH)$_2$-w, (b) LO10, (c) LC10, (d) LCO10 (e) LO5LC5, (f) LO10LCO5, (g) LC10LCO5.
XRD measurements were performed in the range of $2\theta = 10^\circ–150^\circ$. **Figure S4** shows the XRD pattern in the range $2\theta = 10^\circ–150^\circ$. Lattice constants were calculated using the Ca(OH)$_2$ peaks detected in the range $2\theta = 10^\circ–150^\circ$.

**Figure S4.** XRD patterns of all the samples ($2\theta = 10^\circ–150^\circ$).

When lithium compounds were added to calcium hydroxide by the impregnation method, the possible phenomena that may be observed are as follows: (1) Li$^+$ replaces Ca$^{2+}$ (as shown in **Figure S5(a)**), and (2) Li$^+$ locates at the interlayer of the Ca(OH)$_2$ structure (as shown in **Figure S5(b)**). These phenomena may render the calcium hydroxide crystals more fragile and promote the dehydration. Evidence for these hypotheses is inadequate, and further study is required.

**Figure S5.** Schematic diagram of Ca(OH)$_2$ crystal structure: (a) shows phenomenon (1), (b) shows phenomenon (2).
No significant correlation was found between the lattice volume and the dehydration peak temperature; the same was true for the relationship between the lattice volume and the dehydration rate constant. **Figure S6** shows the relationship between the lattice volume and the dehydration peak temperature. **Figure S7** shows the relationship between the lattice volume and the dehydration rate constant.

**Figure S6.** Relationship between lattice volume and dehydration peak temperature.

**Figure S7.** Relationship between lattice volume and dehydration rate constant: (a) lattice volume versus rate constant of zero-order reaction \((k_0)\), (b) lattice volume versus rate constant of first-order reaction \((k_1)\).
All the samples were subjected to a temperature rise test from room temperature to 800 °C and XRD measurement. **Figures S8(a)–(g)** show the XRD pattern of each sample after testing.
Figure S8. XRD pattern of each sample after TG measurement: (a) Ca(OH)$_2$-w, (b) LO10, (c) LC10, (d) LCO10 (e) LO5LC5, (f) LO10LCO5, (g) LC10LCO5.