Dehydration Behavior of Metal-salt-added Magnesium Hydroxide as Chemical Heat Storage Media

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The dehydration behaviors of metal-salt-added magnesium hydroxide as chemical heat storage media were studied. Dehydration temperature of magnesium hydroxide, which was corresponding to heat storage temperature, was dropped from 277 to 233 °C by addition of lithium chloride. The heat storage capacity of 6.8 wt % $LiCl/Mg(OH)_2$ (816 MJ m^{-3}) was 11 times as high as one of authentic $Mg(OH)_2$ under the heat storage operation at 280 °C.

In recent years, the technologies of chemical heat pump and chemical heat storage are widely studied for the reduction of energy consumption and CO_2 emission. If unutilized thermal energy such as industrial waste heat (e.g., the heat around 200 °C from disposal furnaces, the heat around 300 °C from cogeneration systems and so forth) can be recovered and utilized, it will contribute to solve these problems. Thus, chemical heat storage material that can be used at around 200–300 °C should be developed. In view of environmental impact and the temperature of heat source, water adsorption on silica-gel,[1–3] hydration reaction of metal salt,[1,2,4,5] and hydration reaction of metal oxide[1,2,6–8] are promising reactions among the various chemical heat-pump systems and chemical heat-storage materials. A chemical heat-pump system with the reaction between water vapor and magnesium oxide has been reported by our group.[7,8]

$$MgO(s) + H_2O(g) \rightleftarrows Mg(OH)_2(s) \quad \Delta H^\circ = -81\,\mathrm{kJ\,mol^{-1}}$$

In this system, dehydration of magnesium hydroxide as an operation for heat storage would proceed at around 250 °C thermodynamically; however, thermal energy above 350 °C is required for the reaction practically. Thus, some modification of this material is required to be applicable to heat utilization below 300 °C. In this work, dehydration behaviors of metal-salt-added magnesium hydroxides as materials for chemical heat storage were studied to drop the practical dehydration temperature of magnesium hydroxide. The possibility of these materials as new chemical heat-storage media is discussed.

Metal-salt-added magnesium hydroxides were prepared by conventional impregnation method. Three types of metal salt, $LiCl{\cdot}H_2O$ (99.9%; Wako Pure Chemical Industries, Ltd. (WPCI)), NaCl (99.5%; WPCI), $CaCl_2{\cdot}2H_2O$ (99.9%; WPCI) were used as additives. These metal salts were chosen in view of thermal stability and hydrophilicity. Magnesium hydroxide (0.07 µm of diameter, 99.9%; WPCI) was impregnated with aqueous metal salt solution, evaporated at 40 °C with a rotary evaporator, and dried at 120 °C overnight. Here the molar ratio of metal salt to $Mg(OH)_2$ was fixed at 1:10 or 1:50. Here, metal-salt-added magnesium hydroxide is written as $LiCl/Mg(OH)_2$ below. The measurement of dehydration temperature of samples were carried out from 130 to 400 °C with 5 °C min^{-1} of temperature-ramping rate by thermogravimetric method, under evacuated condition below 0.1 kPa. The sample was charged into a Pt cell of the thermogravimetric balance (TGD9600; ULVAC-Riko) as hydroxide state. Before the measurement, sample was dried at 130 °C for 10 min for removing physically adsorbed water. For the hydration reaction test, the sample was charged into a Pt cell of the thermogravimetric balance as hydroxide state. The cell was heated up to the temperature of dehydration operation (T_d) at 280 °C with 20 °C min^{-1} of temperature-ramping rate and kept at the temperature for 30 min with 100 mL min^{-1} of Ar flow as dehydration operation. After that, dehydrated sample in the balance was cooled down to the temperature of hydration operation (T_h) at 110 °C with 100 mL min^{-1} of Ar flow, and water vapor with 57.8 kPa of partial pressure (P_{H_2O}) carried with Ar flow was introduced in the balance for 80 min as hydration operation. After hydration operation, vapor supply was stopped, dry Ar gas was supplied at the same temperature to remove physically adsorbed water on the sample for 20 min, and the second dehydration operation was carried out by heating up the sample to 280 °C. The reacted fraction, x (molar fraction of $Mg(OH)_2$ in the sum of $Mg(OH)_2$ and MgO) was calculated from the initial weight of sample and its weight change.[8]

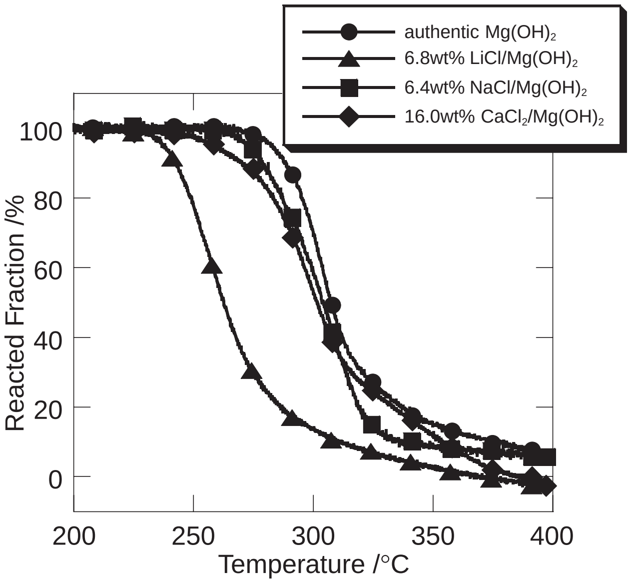

Figure 1. Dehydration behaviors of metal-salt-added magnesium hydroxides under evacuated condition. Molar ratio of metal salts to magnesium hydroxide were fixed at 1:10.

Dehydration behavior of metal-salt-added magnesium hydroxides between 200 and 400 °C are shown in Figure 1. Dehy-

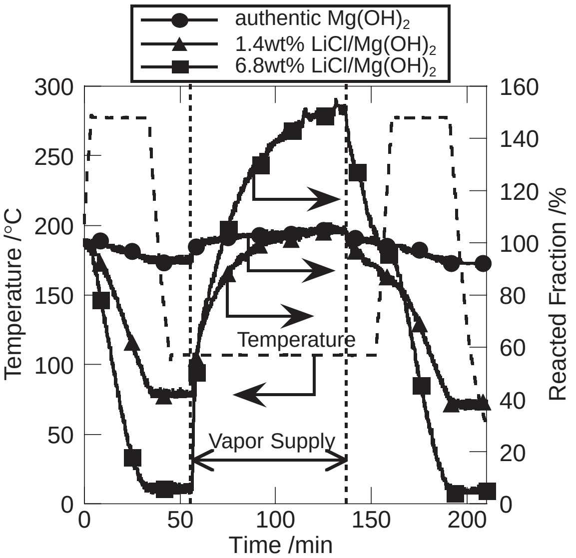

Figure 2. Dehydration and hydration behaviors of authentic $Mg(OH)_2$ and $LiCl/Mg(OH)_2$ ($T_d = 280\,°C$, $T_h = 110\,°C$, $P_{H_2O} = 57.8\,kPa$).

dration of authentic $Mg(OH)_2$ was started from about 277 °C, and the reacted fraction reached 6.4% at 400 °C. On the other hand, dehydration of 6.8 wt % $LiCl/Mg(OH)_2$, 6.4 wt % $NaCl/Mg(OH)_2$, and 16.0 wt % $CaCl_2/Mg(OH)_2$ were started from 233, 267, and 271 °C, respectively. And the reacted fraction of these samples reached 0–5%. Dehydration of hydrated form of authentic LiCl, NaCl, and $CaCl_2$ was completed generally below 200 °C;[9] therefore, these results indicated that dehydration temperature of $Mg(OH)_2$ was shifted to a lower temperature by metal salt addition.

Figure 2 shows the dehydration and hydration behavior of authentic $Mg(OH)_2$ and two kinds of $LiCl/Mg(OH)_2$. The reacted fraction of authentic $Mg(OH)_2$ reached 93.3% after dehydration operation at 280 °C. This result means that only 6.7% of water was dehydrated from $Mg(OH)_2$. The reacted fraction of 6.8 wt % $LiCl/Mg(OH)_2$ reached 6.0% after dehydration operation. This result means also that 94.0% of water was dehydrated from $Mg(OH)_2$ and that heat is stored as oxide state in this amount. By the hydration operation, reacted fraction of 6.8 wt % of $LiCl/Mg(OH)_2$ reached 154%, and it decreased 95.4% after stopping of vapor supply. According to the result of this hydration period, it can be suggested that three types of reaction, hydroxide formation of MgO, hydrate formation of LiCl, and water adsorption on the sample surface are occurred. Finally, reacted fraction of this sample decreased to 4.4% by second dehydration operation at 280 °C. The reacted fraction of 1.4 wt % $LiCl/Mg(OH)_2$ reached to 41.8% after dehydration operation at 280 °C. This result means that the amount of LiCl as additive was not enough to enhance the dehydration of $Mg(OH)_2$. These results indicates that $LiCl/Mg(OH)_2$ is suitable for chemical heat-storage operation at 280 °C in comparison with authentic $Mg(OH)_2$ having lower dehydration amount.

The estimated thermal storage capacity of $LiCl/Mg(OH)_2$ and mixed hydroxides are summarized in Table 1.[8] Thermal storage capacities were calculated from the reaction heat and measured conversion of hydroxide formation, adsorption heat of water vapor on sample, and amount of adsorbed water. In the estimations for $LiCl/Mg(OH)_2$, hydration amount of LiCl could not be separated from the amount of adsorbed water, thus it was included into the amount of adsorbed water. The capacity of authentic $Mg(OH)_2$ was small ($126\,kJ\,kg^{-1}$) under the dehydration operation at 280 °C. On the other hand, the capacities of $LiCl/Mg(OH)_2$ were higher than that of $Mg(OH)_2$. Especially, that of 6.8 wt % $LiCl/Mg(OH)_2$ was estimated as $1360\,kJ\,kg^{-1}$. These results mean that lithium chloride addition is expected to be effective for the reactivity enhancement of $Mg(OH)_2$ at lower than 300 °C.

Table 1. Thermal storage capacity of lithium-chloride-added magnesium hydroxide and magnesium-containing mixed hydroxides ($T_d = 280\,°C$, $T_h = 110\,°C$, $P_{H_2O} = 57.8\,kPa$)

Sample	Heat storage capacity[8]	
	$/kJ\,kg^{-1}$	$/MJ\,m^{-3}$ [b]
Authentic $Mg(OH)_2$	126	75.6
1.4 wt % $LiCl/Mg(OH)_2$	742	445
6.8 wt % $LiCl/Mg(OH)_2$	1360	816
$Mg(OH)_2$[a]	24.5	14.7
$Mg_{0.5}Ni_{0.5}(OH)_2$[a]	165	99.0
$Mg_{0.5}Co_{0.5}(OH)_2$[a]	358	215

[a]Prepared by coprecipitation method (ref 8). [b]Density of samples were assumed as $0.6\,g\,cm^{-3}$.

It is concluded that metal-salt-added magnesium hydroxides are more suitable for chemical heat storage with hydration reaction for thermal energy at lower than 300 °C than the authentic magnesium hydroxide. The sample stability against multiple operations of hydration and dehydration, reaction mechanism, reaction heat under practical condition should be studied further.

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