doi:10.1246/cl.2012.583

Dehydration and Hydration Behavior of Rare-earth Hydroxides for Chemical Heat Pumps

Hirokazu Ishitobi,[1] Junichi Ryu,*[2] and Yukitaka Kato[2]
[1]*Department of Nuclear Engineering, Graduate School of Science and Engineering,*
Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550
[2]*Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology,*
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550

(Received February 8, 2012; CL-120105; E-mail: cyliu@nr.titech.ac.jp)

Pure and mixed rare-earth hydroxides are expected to be new materials for chemical heat pumps. In this study, the dehydration and hydration behavior of these materials was investigated by thermogravimetry. The dehydration temperature could be lowered by increasing the Nd or Gd ion content in the hydroxides. $La_{0.50}Gd_{0.50}(OH)_3$ is an ideal candidate material for chemical heat pumps that can store thermal energy at 300 °C; further, heat output can be generated from the heat source at 40 °C.

Development of energy-saving technologies is necessary to overcome problems related to global energy-resource depletion. A chemical heat pump (CHP), which converts thermal energy into chemical energy and stores energy for a long period, is a promising solution to the above-mentioned problems. Our group proposed a CHP based on a magnesium oxide/water system.[1] The dehydration and hydration reactions correspond to heat storage and heat output operations, respectively.

$$Mg(OH)_2(s) \rightleftarrows MgO(s) + H_2O(g) \quad \Delta_r H^\circ = 81.0\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

CHPs based on mixed hydroxides such as magnesium–cobalt and magnesium–nickel hydroxides can store thermal energy at 280 °C.[2] However, they require saturated water vapor at 85 °C for the heat output operation. Hence, it is necessary to develop new materials that can be used at a low water vapor pressure (low heat source temperature) during the heat output operation. Yamamoto et al. reported that the first dehydration of rare-earth hydroxides proceeds at approximately 300 °C.[3] Nagao et al. reported that La_2O_3 shows high hydration reactivity at 25 °C.[4] However, a technical problem is that the first dehydration temperature of $La(OH)_3$, which is about 320 °C,[5] is not suitable for the storage of industrial waste heat. The dehydration and hydration reactivity of rare-earth mixed hydroxides can be controlled by modifying the metal ion composition. Thus, mixed rare-earth hydroxides are considered candidate materials for CHPs. The dehydration reaction of a rare-earth hydroxide ($Ln(OH)_3$) is expressed as follows:

$$Ln(OH)_3(s) \rightleftarrows LnOOH(s) + H_2O(g) \tag{2}$$

$$LnOOH(s) \rightleftarrows \frac{1}{2}Ln_2O_3(s) + \frac{1}{2}H_2O(g) \tag{3}$$

For example, the enthalpy changes for the first and second dehydration of $La(OH)_3$ are 95.0 and 60.8 kJ mol^{-1}, respectively. Another energy-saving technology is a adsorption heat pump (AdHP). Kakiuchi et al. reported a Fe-contained $AlPO_4$-based AdHP system for air conditioning.[6] They can input heat (regeneration of adsorbent) at lower than 100 °C, which is different from our research subject.

Pure and mixed rare-earth hydroxides ($La(OH)_3$, $La_{0.50}Nd_{0.50}(OH)_3$, $Nd(OH)_3$, $La_{0.50}Gd_{0.50}(OH)_3$, and $Gd(OH)_3$) were prepared by the precipitation or coprecipitation method. $La(NO_3)_3\cdot 6H_2O$ (99.9%, Wako Pure Chemical Industries, Ltd. (WPCI)), $Nd(NO_3)_3\cdot 6H_2O$ (99.5%, WPCI), and $Gd(NO_3)_3\cdot 6H_2O$ (99.5%, WPCI) were used as precursors of the hydroxides. An aqueous solution of the rare-earth nitrate(s) was added to 1 M aqueous NaOH solution. The resulting precipitates were washed five or more times with pure water and thermally decomposed by heating at 800 °C for 5 h. Hydrothermal treatment was performed under the following conditions: 160 °C, 24 h for $Gd(OH)_3$ and 120 °C, 3 h for the other hydroxides. $Mg(OH)_2$ (0.07 µm, 99.9%, WCPI) was used as reference. X-ray diffractometry (XRD) measurements were carried out using an Ultima IV diffractometer (Rigaku Corporation) over the 2θ range 10–90° at a scan speed of 0.5° min^{-1}. Monochromatic Cu Kα radiation was used, and the generator voltage and current were 40 kV and 40 mA, respectively. The thermal decomposition curves for the samples were measured by thermogravimetry (TG) using a TGD9600 thermobalance (Ulvac-Riko Inc.). Before the analysis, the samples were dried at 120 °C for 30 min to remove the physically adsorbed water. The samples were heated to 400 °C at the rate of 5 °C min^{-1} under argon gas flow (flow rate: 100 mL min^{-1}). Then the dehydration–hydration behavior of the samples was determined by TG. The dehydration operation was carried out at 300 °C ($T_d = 300$ °C) for 30 min, and the hydration operation was performed at 110 °C ($T_h = 110$ °C) for 80 min. During hydration operation, a mixture of water vapor and argon (carrier gas) at a water vapor pressure (p_{H_2O}) of 7.4 kPa was introduced. This vapor pressure corresponds to saturated water vapor pressure at 40 °C. After the hydration operation had completed, the vapor supply was stopped, and dry argon gas was introduced at the same hydration operation temperature (110 °C) for 50 min to remove the physically adsorbed water (drying operation). The dehydration–hydration–drying operation was carried out at heating and cooling rates of 20 °C min^{-1} and at an argon gas flow rate of 100 mL min^{-1}. The mole fraction of the hydroxide was calculated from the weight change in the samples.

$$X[\%] = \left[1 + \frac{\Delta w/(n\cdot M_{H_2O})}{w_{ini}/M_{hydroxide}}\right]\cdot 100 \tag{4}$$

Here, Δw is the weight change in the sample [g]; n, the stoichiometric factor [—] (1 for $Mg(OH)_2$; 1.5 for pure and mixed rare-earth hydroxides); M_{H_2O}, the molecular weight of water [g mol^{-1}]; $M_{hydroxide}$, the molecular weight of the pure or mixed hydroxide [g mol^{-1}]; and w_{ini}, the initial sample weight [g]. For rare-earth compounds, $X = 100\%$, 33.3%, or 0% would imply that the sample is a pure hydroxide, oxyhydroxide, or pure oxide, respectively. In this study, the temperature at which the differential thermogravimetric (DTG) curve shows a maximum defined as the first dehydration reaction temperature (T_f). The mole

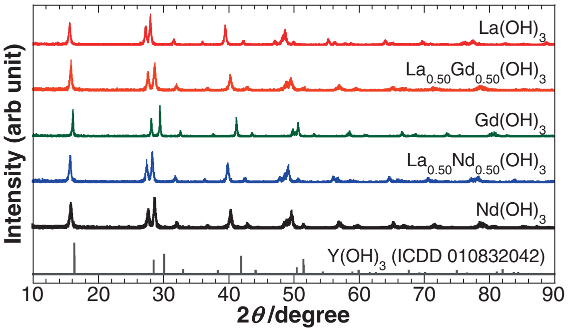

Figure 1. XRD patterns for pure and mixed rare-earth hydroxides and reference ($Y(OH)_3$).

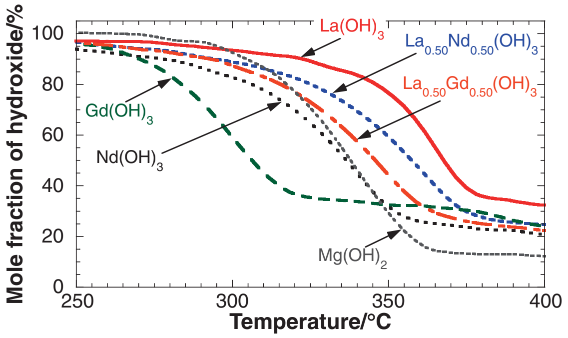

Figure 2. Thermal decomposition curves for pure and mixed rare-earth hydroxides and $Mg(OH)_2$.

fractions of the hydroxide after the dehydration and drying operations are designated as X_d and X_c, respectively. The conversion in the hydration (ΔX_h) is defined as $\Delta X_h = X_c - X_d$.

The XRD patterns for the samples and the reference ($Y(OH)_3$, ICDD 010832042) are shown in Figure 1. All the samples showed the $Y(OH)_3$-type structure. The peaks for the mixed hydroxides were not separated into individual $La(OH)_3$, $Nd(OH)_3$, and $Gd(OH)_3$ peaks. The peak positions shifted to the higher-angle side when the Nd or Gd ion composition was increased, indicating that the samples were pure or mixed $Y(OH)_3$-type hydroxides. The thermal decomposition curves for the samples are shown in Figure 2. The dehydration temperature was lowered when the Nd or Gd ion composition in the mixed rare-earth hydroxide was increased. The effect of the Gd ion content on the temperature shift for dehydration was greater than that of the Nd ion content. T_f's were 368, 348, 302, and 340 °C for $La(OH)_3$, $La_{0.50}Gd_{0.50}(OH)_3$, $Gd(OH)_3$, and $Mg(OH)_2$ respectively. The dehydration reactivity could be controlled by adjusting the metal ion composition in the mixed hydroxide. Figure 3 shows the dehydration–hydration behavior of the samples. Dehydration of $La(OH)_3$, $La_{0.50}Nd_{0.50}(OH)_3$, $Nd(OH)_3$, $La_{0.50}Gd_{0.50}(OH)_3$, and $Mg(OH)_2$ did not proceed to completion even upon heating at 300 °C for 30 min. On the other hand, X_d value was 34% for $Gd(OH)_3$, suggesting that the first dehydration (eq 2) had proceeded in the case of $Gd(OH)_3$ under the above-mentioned conditions. $La(OH)_3$ and $La_{0.50}Nd_{0.50}(OH)_3$ are expected to undergo hydration readily, i.e., they should have high hydration reactivity, because their X_c values were 90% and 84%, respectively. The low dehydration reactivity of these hydroxides should make their ΔX_h values low. The ΔX_h values of $Gd(OH)_3$ and $Mg(OH)_2$ were relatively low, 2.5% and 6.2%, respectively. The hydration reactivity of these two hydroxides was low at 110 °C and a water vapor pressure of 7.4 kPa, making them unsuitable for use as CHP materials under these conditions. $La_{0.50}Gd_{0.50}(OH)_3$ had the highest ΔX_h (20%) and was suitable for use in CHPs driven by saturated water vapor at 40 °C.

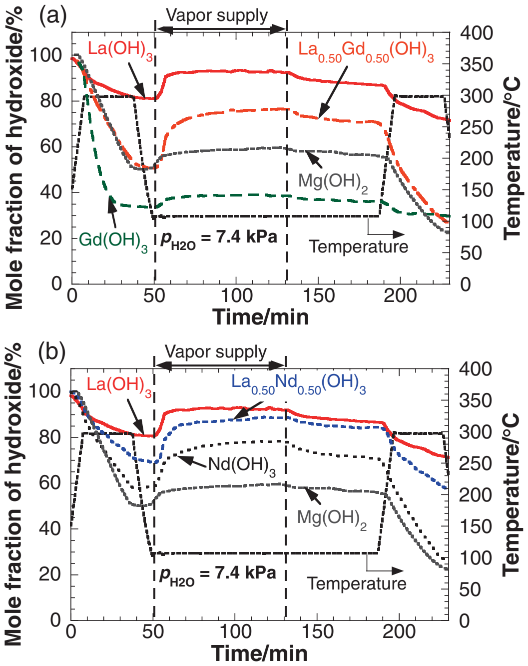

Figure 3. Dehydration and hydration behavior of pure and mixed rare-earth hydroxides; (a) $La(OH)_3$, $La_{0.50}Gd_{0.50}(OH)_3$, $Gd(OH)_3$, and $Mg(OH)_2$; (b) $La(OH)_3$, $La_{0.50}Nd_{0.50}(OH)_3$, $Nd(OH)_3$, and $Mg(OH)_2$ ($T_d = 300$ °C, $T_h = 110$ °C, $p_{H_2O} = 7.4$ kPa).

In conclusion, we propose rare-earth hydroxides as new candidate materials for CHPs. The dehydration reactivity of the hydroxides can be controlled by adjusting the metal ion composition. CHPs based on $La_{0.50}Gd_{0.50}(OH)_3$ can store thermal energy at 300 °C, and heat output from the heat source can be triggered at 40 °C. The conventional material ($Mg(OH)_2$) cannot be used under these conditions.

This research was supported by the Industrial Technology Research Grant Program in 2008 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. The authors are grateful to this foundation.

References

1 Y. Kato, N. Yamashita, K. Kobayashi, Y. Yoshizawa, *Appl. Therm. Eng.* **1996**, *16*, 853.
2 J. Ryu, R. Takahashi, N. Hirao, Y. Kato, *J. Chem. Eng. Jpn.* **2007**, *40*, 1281.
3 O. Yamamoto, Y. Takeda, R. Kanno, M. Fushimi, *Solid State Ionics* **1985**, *17*, 107.
4 M. Nagao, H. Hamano, K. Hirata, R. Kumashiro, Y. Kuroda, *Langmuir* **2003**, *19*, 9201.
5 A. Neumann, D. Walter, *Thermochim. Acta* **2006**, *445*, 200.
6 H. Kakiuchi, S. Shimooka, M. Iwade, K. Oshima, M. Yamazaki, S. Terada, H. Watanabe, T. Takewaki, *Kagaku Kogaku Ronbunshu* **2005**, *31*, 361.