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Formation and decomposition of some rare earth (RE = La, Ce, Pr) hydroxides and oxides by homogeneous precipitation

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Abstract

Formation and thermal decomposition of rare earth (RE = La, Ce, Pr) hydroxides and oxides by homogeneous precipitation using hexamethylenetetramine. The precipitatates were examined using thermal gravimetry and differential thermal analysis, infrared spectrometry and X-ray diffraction. The as-precipitated powders from the present process were $La(OH)_3$, CeO_2, $Pr(OH)_3$. In the case of Ce, a cubic fluorite phase of cerium dioxide was directly obtained. The lanthanum trihydroxide decomposed to oxides via three steps. Two-step dehydration decomposition behavior at 340 and 500 °C was observed as $La(OH)_3 \rightarrow LaOOH + H_2O$ and $2LaOOH \rightarrow La_2O_3 + H_2O$. The activation energy (ΔH) for dehydration was 240 and 244 kJ/mol, respectively. The additional decomposition of carbonate-containing species was observed at 670 °C with ΔH of 390 kJ/mol. $Pr(OH)_3$ did not show additional TGA profile of carbonate decomposition. Since no carbonate species form in solution during the HMT precipitation (hydrolysis of this molecule), the difference between La and Pr depends on the strength of basicity in the reaction with CO_2 after precipitation.

Keywords: La; Ce; Pr; Precipitation; Decomposition

1. Introduction

Precipitation technique of rare earth compounds from aqueous solution using some reagents is useful for the development of nanoparticles of oxides for the application such as ceramics and catalysts. Homogeneous precipitation method, which is based on acid-base reaction, is conventional for preparing such functional rare earth oxides from a view point of industrial application as well as a lab-scale experiment [1–4]. This paper describes some results of precipitates from homogeneous precipitation process using hexamethylenetetramine and their thermal change. Rare earth (RE = La, Ce, Pr) hydroxides and oxides by homogeneous precipitation were examined using thermal gravimetry analysis (TGA), differential thermal analysis (DTA), infrared spectrometry (IR) and X-ray diffraction (XRD) methods.

2. Experimental

The precipitates were obtained from aqueous rare earth (RE) nitrate (RE = La, Ce, Pr, 99.9%, Kojundo-kagaku, Japan) through homogeneous precipitation. Two aqueous solutions of 0.1 M metal nitrate and 0.06 M hexamethylenetetramine (HMT) were prepared by the process dissolving in distilled water, and then they were mixed with each other with stirring for 0.5 h. The mixed solution was heated up to 95 °C, then the precipitates formed in solution during the heat procedure, and then held with stirring for 1 h in air. The powder was obtained by filtering the solutions, and washed with water twice, and then dried at 110 °C over night. The XRD data of powder samples were obtained using a Rigaku rint-2000 powder diffractometer with Cu Kα source. Scanning electron microscopy (SEM), Jeol-JMS6000 was applied to observe the morphology of precipitates. The TGA and DTA measurements were performed by a Mac-science model 2000s. The IR spectra of pressed disks of

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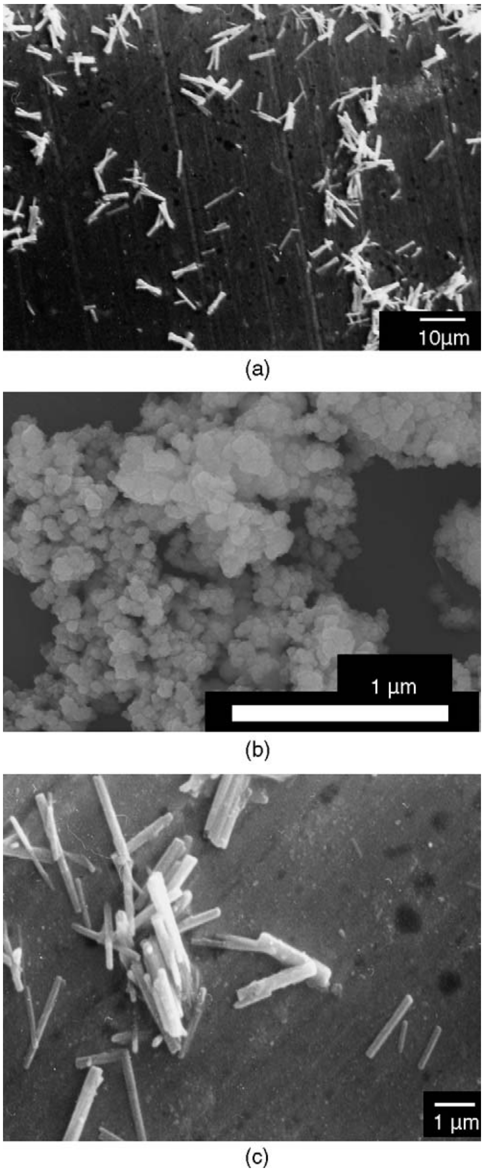
powders mixed with KBr were recorded by Nicolet Impact 400.

3. Results and discussion

The precipitates of La and Pr were identified as hexagonal trihydroxide, $La(OH)_3$ and $Pr(OH)_3$, respectively. In the case of Ce, a cubic fluorite phase of cerium dioxide CeO_2 was directly obtained. The morphology of $La(OH)_3$ and $Pr(OH)_3$ was rod-like, and CeO_2 was the aggregate of spherulic small precipitates, as shown in Fig. 1. CeO_2 maintained its cubic structure, with a slight decrease of weight at around 100–150 °C due to adsorbed water on fine particle, at temperatures up to 1200 °C [5]. $Pr(OH)_3$ quantitatively decomposed to PrOOH at as low temperature as 400 °C, and then Pr_2O_3 at 700 °C. However, $La(OH)_3$ decomposed with three steps of weight decrease during heat treatment at temperatures up to 1200 °C. In present work, we have examined the process of decomposition of $La(OH)_3$ from HMT homogeneous precipitation.



(a)

(b)

(c)

Fig. 1. SEM photograph of precipitates from homogeneous precipitation: (a) $La(OH)_3$, (b) CeO_2, (c) $Pr(OH)_3$.

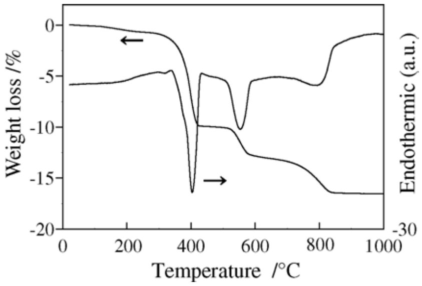


Fig. 2. DTA and TGA profiles of $La(OH)_3$ from HMT homogeneous precipitation.

The DTA and TGA profiles of prepared $La(OH)_3$ powders from room temperature to 1200 °C are illustrated in Fig. 2. On the TGA curve, there was a slight decrease at 100 °C due to adsorbed water on powder, and then a large weight loss was observed to start at 350 °C, then two smaller decreasing steps at 500 and 670 °C. The total weight loss was 16%, and each loss was 10% (the first), 3% (the second) and 3% (the third). The corresponding endothermic peaks on the DTA curve appears at 350–410, 500–580, and 670–810 °C. The weight loss and endothermic reactions suggested the decomposition reactions of the compound or mixture. The XRD patterns of a starting powder and the heated powders are illustrated in Fig. 3. The as-precipitated sample is $La(OH)_3$ with well-developed crystallinity. The powder was heated at each temperature in air at heating rate of 10 K/min and rapidly cooled (corresponding to TGA). At 200 °C, the sample retained the original crystal phase, although a slight weight decrease appeared in TGA. After heating at 400 °C, LaOOH formed, as in Fig. 2, however it seemed to consist of small crystalline domain as indicated by broad and weak intensities of XRD peaks.

Several workers examined the strange thermal decomposition of $La(OH)_3$ [6–13]. Fricke [6] reported the formation of LaOOH from $La(OH)_3$. LaOOH was examined as a stable structure with monoclinic symmetry [7–12]. The broad and weak intensities of the XRD for our sample heated at 560 °C was similar to the reported intensities of a phase (LaOOH) by Shafer and Roy who examined the system of rare earth oxide and water [13]. However, their identification was actually not certain. So, we measured the infrared spectra to identify functional group for a series of heated samples. The strong band at 3610 cm^{-1} was observed, corresponding to OH stretching frequency, for all samples. The OH deformation mode was observed at 670 cm^{-1} (610–740 cm^{-1}) as broad spectra for both powders as-prepared and heated at 200 °C. The OH deformation band was detected at as lower frequency as 660 cm^{-1} (620–710 cm^{-1}) in a sample heated at 400 °C, which seemed to represent OH in LaOOH. The broad features

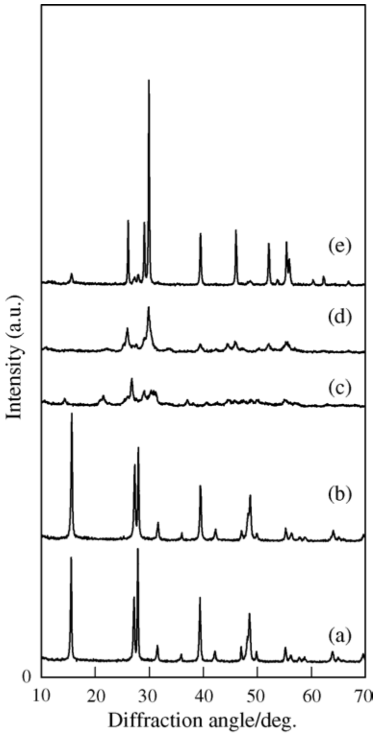


Fig. 3. XRD patterns of a starting $La(OH)_3$ powder (a), and the heated powders at 200 °C (b), 400 °C (c), 560 °C (d), and 1000 °C (e).

represented the disorder of protons in these crystals, even if they showed clear XRD patterns, as discussed in the previous paper using neutron spectra [14]. In addition, in the samples heated at 400 and 600 °C, characteristic sharp peaks of CO_3^{2-} was observed at 850, 1085, 1385, and 1460 cm^{-1} [15]. The data suggest the reaction with CO_3^{2-} species on the powders after heat treatment at these temperatures. Therefore, the most likely identification to the third step is the decomposition of surface carbonate, as suggested by Rosynek and Magnuson [10] for fine catalytic lanthanum oxide powders. Since lanthanum is basic element, its oxide and hydroxide can react with CO_2 in air to form carbonate that is not so crystalline. After the heat treatment of the precipitate at 560 °C, the XRD peak intensities of as-mentioned unknown phase are actually very similar to those of La_2O_3. In the temperature range over 550 °C, monoclinic LaOOH should decompose to oxide, so that the sample consists of La_2O_3 as a major phase. After the elimination of these peaks of La_2O_3, in the XRD of a sample heated at 560 °C, the peaks were signed with small intensities at 0.405, 0.355, 0.265, and 0.205 nm, which seemed to correspond to those of $LaCO_3OH$. Saksonova et al. [11] examined such carbonated $La(OH)_3$ using several methods, however suggested amorphous $La_2(OH)_4CO_3$ as a final product before the complete decomposition to La_2O_3.

It should be noted that $Pr(OH)_3$ did not show such additional TGA profile (the third decomposition step) even by the same handling process for precipitates in present work. Since no carbonate species form in a solution through the HMT precipitation process, the original metal hydroxide should not contain carbonate-related compounds. Thus, the difference between two elements (La and Pr) depends on the strength of basicity in the reaction with CO_2 after precipitation.

The decomposition reactions of $La(OH)_3$ in the first and second steps were concluded as

$$La(OH)_3 \rightarrow LaOOH + H_2O \tag{1}$$

$$2LaOOH \rightarrow La_2O_3 + H_2O \tag{2}$$

For these reactions, we measured the activation energies (ΔH) of reaction using the convenient relationship of decomposition temperature versus heating rate (Kissinger plot [16]) in the TGA data. Fig. 4 shows the Kissinger plots for three decomposition reactions. ΔH was 240 (±10) kJ/mol for a reaction (1), and 244 (±10) kJ/mol for a reaction (2). For the third decomposition, ΔH was 390 (±20) kJ/mol. For the first and second steps, both reactions are essentially dehydration from different hydroxides, $La(OH)_3$ and LaOOH, respectively. Kissinger [16] examined the enthalpies for hydration reaction of lanthanide oxides through thermochemical approach, and determined $\Delta H = 360$ kJ/mol for the dehydration of $La(OH)_3$ to La_2O_3. Since the lattice energy for each crystal should be considered for the calculation of total enthalpy for a decomposition reaction, the careful discussion must be required as precise thermodynamics. However, we can provide, in this work, the experimental values of ΔH from two independent reactions that may be estimated with good accuracy as following description. For a total dehydration reaction of $La(OH)_3$ to a final oxide, we can use two values, obtained from the plots in Fig. 4, by neglecting the difference of Madelung constants between two crystals $La(OH)_3$ and LaOOH. The difference of Madelung constants should be far smaller that the enthalpy of the decomposition reaction itself (i.e. the destruction of the lattice). If ΔH (240 kJ/mol) for a reaction (1) is added by a half of the second ΔH (244 kJ/mol) for a reaction (2) per molar La species, we obtained that the resultant value for a total decomposition reaction via two steps is 362 kJ/mol, that is consistent with 360 kJ/mol as a total enthalpy for full dehydration in the previous reference

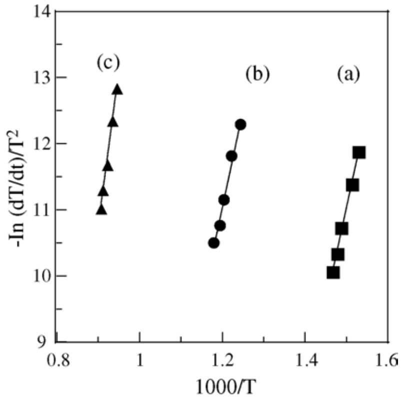


Fig. 4. Kissinger's plots for three decomposition reactions of $La(OH)_3$ powder in present work: (a) the first, (b) the second, and (c) the third step.

[17]. Meanwhile, the third reaction should partially contain the decomposition of carbonate species, so that at the least, the fact that ΔH is larger than that of pure dehydration is suggested. This should be explained by the difference in the bonding strength of OH^- and CO_3^{2-} with La^{3+}. We have provided, in present work, the measured value of temperature and enthalpy for two dehydration reactions of lanthanum hydroxides $La(OH)_3$ and LaOOH.

4. Summary

Formation and thermal decomposition of rare earth RE (RE = La, Ce, Pr) hydroxides and oxides by homogeneous precipitation. The precipitates from the present process were $La(OH)_3$, CeO_2, $Pr(OH)_3$. In the case of Ce, a cubic fluorite phase of cerium dioxide was directly obtained. The lanthanum trihydroxide decomposed to oxides via three steps. Two-step dehydration decomposition was observed in this study; $La(OH)_3 \rightarrow LaOOH + H_2O$ and $2LaOOH \rightarrow La_2O_3 + H_2O$. The temperature and activation energy were measured for each decomposition step; at 340 °C and 240 kJ/mol, and at 500 °C and 244 kJ/mol, respectively. The additional decomposition of carbonate-containing species was observed at 670 °C and 390 kJ/mol. $Pr(OH)_3$ did not show such additional TGA profile of carbonate decomposition. The difference between La and Pr depends on the strength of basicity in the reaction with CO_2 after precipitation.

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