SYNTHESIS, ACID AND BASE RESISTANCE OF NICKEL - CERIUM (+III) PHOSPHATE PIGMENTS

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Abstract: Transition metal phosphates are used as inorganic pigments, however these materials had a weak point for acid and base resistance. Because cerium phosphate is insoluble in acidic and basic solution, the addition of cerium was tried to improve the acid and base resistance of nickel phosphate pigment. The cerium doped nickel phosphates were prepared from phosphoric acid, nickel nitrate, and cerium nitrate solution. The additional effects of cerium cation were studied on the chemical composition, particle shape and size distribution, specific surface area, color, acid and base resistance of the precipitates and their thermal products.

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INTRODUCTION

Phosphates have been used for ceramic materials, catalysts, fluorescent materials, dielectric substances, metal surface treatment, detergent, food additives, fuel cells, pigments, etc.1-3. Especially, as a pigment, these materials have good anticorrosion properties for oxidation reaction and suitable for coating.4-7. However, there is a weak point that is a certain degree of solubility for acidic and basic solution.

It is well known that rare earth phosphates are insoluble for acidic and basic solution in the groups of phosphate materials. In general, the addition of rare earth elements gives higher functional properties to the material.8 Consequently, the addition of rare earth cation had the anticipation to improve the acid and base resistance of inorganic phosphate pigments. In previous work, the addition of rare earth cation was studied in solid state syntheses and powder properties, acid and base resistance of cobalt orthophosphate, pyrophosphate, and cyclo-tetraphosphate.3 The chemical composition and powder properties of thermal products were changed by the addition of rare earth cation. Furthermore, this addition improved the acid and base resistance of phosphate materials synthesized in solid state reaction.

For the syntheses of inorganic phosphates, there are some methods, one is based on the solid state reaction, another one is on the cation exchange reaction in aqueous solution, and others. The method by the solid state reaction had some merits to be easy to form condensed phosphate and to control the molar ratio of cation / phosphorus, on the other hand, had a demerit to be difficult to keep the homogeneity of materials. The preparation of transition metal phosphate in aqueous solution had an advantage to obtain the homogenized materials and various kinds of metal phosphates. However, it had a weak point to be difficult to control the molar ratio of cation / phosphorus. The synthetic method had much influence on the properties of phosphate materials. There are some cases that the phosphate prepared in aqueous solution has the different properties with the phosphate synthesized in solid state reaction. It is important to clear the additional effects of rare earth cation on syntheses of inorganic phosphate materials prepared in wet process and their properties.

The substitution with lanthanum in nickel and cobalt phosphate materials prepared in wet process was studied on the chemical composition, powder condition, color, acid and base resistance.9,10 Specific surface area of phosphates increased and particle size became larger by the substitution with lanthanum. The substitution with lanthanum was effective on acid and base resistance for design of inorganic phosphate pigment. Cerium cation is also one of rare earth cation. However, the different phenomena are expected with lanthanum cation, because cerium cation has stable tri- and tetra-valent states.

In this work, nickel – cerium phosphates were synthesized in aqueous solution. The obtained products were estimated from their particle shape and size distribution, specific surface area, color, acid and base resistance.
base resistance.

EXPERIMENTAL

The 0.1 mol/l of nickel nitrate, Ni(NO₃)₂, solution was mixed with 0.1 mol/l of phosphoric acid solution in the molar ratio of Ni/P=3/2. This ratio is settled from the chemical composition of nickel orthophosphate, Ni₃(PO₄)₂. The certain part of nickel nitrate was substituted with cerium nitrate, Ce(NO₃)₃, in the molar ratio of Ni/Ce=10/0, 9/1, 8/2, 5/5, 2/8, and 0/10. For the valence balance, three nickel cations were replaced with two cerium cations. Finally, the solutions were mixed in the molar ratio of Ce/P=1/1. Then, the mixed solution was adjusted to pH 7 by ammonia solution. The precipitate was filtered off and dried in air condition.

A part of the precipitates was dissolved in hydrochloric acid solution. The ratios of phosphorus and cerium in the precipitates were also calculated from ICP results of these solutions, using SPS1500VR, Seiko Instruments Inc. The thermal behavior of these materials was analyzed by TG-DTA and XRD. TG and DTA curves were measured with a Shimadzu DTG-60H at a heating rate of 10 °C/min under air. XRD patterns were recorded on a Rigaku Denki RINT 1200M X-Ray diffractometer using monochromated CuKα radiation.

The powder properties of thermal products at 200, 400, 600, and 800°C were characterized by particle shape, particle size distribution, specific surface area, and their color. Particle shapes were observed by scanning electron micrographs (SEM) using JGM-5510LV, JEOL Ltd. Particle size distribution was measured with laser diffraction / scattering particle size distribution HORIBA LA-910. Specific surface areas of phosphates were calculated from the amount of nitrogen gas adsorbed at the temperature of liquid nitrogen by BET method with Belsorp mini from BEL JAPAN, INC. The color of phosphate pigments was estimated by ultraviolet - visible (UV-Vis) reflectance spectra with a Shimadzu UV2550.

Furthermore, the acid and base resistance of materials was estimated in following method. The 0.1 g of thermal products was allowed to stand in 100 ml of 0.1 wt% sulphuric acid or 0.1 wt% sodium hydroxide solution for 1 day. Then, solid was removed off by filtration, the solution was dilute with nitric acid for ICP measurement. The concentrations of phosphorus, nickel, cerium cation were calculated by ICP results. As a resistance estimation, the solubility (%) of target elements was calculated to divide by the concentration that thermal products were completely dissolved by hot hydrochloric acid.

RESULTS AND DISCUSSION

CHEMICAL COMPOSITION OF NICKEL = CERIUM PHOSPHATES

TABLE 1 shows chemical composition, NiₓCeᵧHₓPO₄ₓ, of samples synthesized in Ni/Ce ratios from ICP results. This chemical composition was the expedient one to indicate the nickel, cerium, and hydrogen ratios to phosphorus. From the valence of nickel, cerium cations, and phosphate anion, hydrogen ratio was calculated in the following equation.

\[ z(\text{hydrogen ratio}) = 3 - 2x(\text{nickel ratio}) - 3y(\text{cerium ratio}) \]  

(1)

The negative value of z means the existence of hydroxide anion. Sample prepared in Ni/Ce = 10/0 had the near ratio with nickel hydrogenphosphate, NiHPO₄. On the other hand, cerium ratio was enough high at samples prepared in Ni/Ce=0/10. Cerium orthophosphate was considered to form in this condition. In the middle Ni/Ce ratios, cerium ratio was higher than that in preparation process. This tendency was caused from that cerium phosphate is easy to precipitate without pH adjustment by ammonium solution and that formation of nickel phosphate needs pH adjustment.

<table>
<thead>
<tr>
<th>Ni/Ce</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/0</td>
<td>1.064</td>
<td>0</td>
<td>0.872</td>
</tr>
<tr>
<td>9/1</td>
<td>0.674</td>
<td>0.106</td>
<td>1.334</td>
</tr>
<tr>
<td>8/2</td>
<td>0.610</td>
<td>0.233</td>
<td>1.081</td>
</tr>
<tr>
<td>5/5</td>
<td>0.396</td>
<td>0.618</td>
<td>0.356</td>
</tr>
<tr>
<td>2/8</td>
<td>0.174</td>
<td>0.945</td>
<td>-0.183</td>
</tr>
<tr>
<td>0/10</td>
<td>0</td>
<td>1.198</td>
<td>-0.594</td>
</tr>
</tbody>
</table>

Samples without heating indicated XRD peaks of NH₄H₂PO₄. These peaks disappeared with the increase of cerium ratio. Samples prepared in Ni/Ce=10/0 and then heated at 200-600°C were amorphous phase in XRD analyses. Samples containing cerium cation heated at 200-600°C indicated the peaks of Rhabdophane-type CePO₄. FIGURE 1 shows XRD patterns of samples synthesized in various Ni/Ce ratios and then heated at 800°C. Sample prepared in Ni/Ce=10/0 had strong peaks of nickel pyrophosphate, Ni₅P₃O₁₀. The peaks of Monazite-type CePO₄ were observed in XRD.
patterns of Ce-substituted samples.

FIGURE 2 shows DTA curves of nickel – cerium phosphates. DTA curves of sample prepared in Ni/Ce=10/0 had large endothermic peak at 100°C, small endothermic peak at 250 °C, and small exothermic peak at 770°C. These peaks were due to the volatilization of water, dehydration condensation of phosphate, and crystallization of nickel phosphate, respectively. Nickel hydrogenphosphate was condensed to nickel pyrophosphate in following reaction at 250°C.

\[ 2 \text{NiHPO}_4 \rightarrow \text{Ni}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \]  \hspace{1cm} (2)

The substitution with cerium produced the endothermic peaks at 80 and 240°C in DTA curves. These peaks were caused from the volatilization of adsorbed and crystalline water, respectively. FIGURE 3 shows TG curves of samples prepared in various Ni/Ce ratios. Samples prepared in Ni/Ce=10/0 had large weight loss over 50%. Nickel hydrogenphosphate had large amount of adsorbed and crystalline water. By the substitution with cerium cation, this weight loss became small. This was caused from that nickel phosphate had weight loss due to the volatilization of ammonia and dehydration condensation of phosphate, on the other hand, that cerium phosphate did not have these weight losses.

**POWDER PROPERTIES OF NICKEL - CERIUM PHOSPHATES**

FIGURE 4 shows SEM images of samples synthesized in various Ni/Ce ratios and then heated at 400 °C. Sample prepared in Ni/Ce=10/0 had pillar-like particles. By the substitution with cerium, particle shape changed to granule. Same tendency was observed in samples heated at other temperatures. The heating temperature had less influence on particle shape than the ratio of cerium cation.

FIGURE 5 shows the particle size distribution of samples synthesized in various Ni/Ce ratios and then
FIGURE 5  Particle size distribution of samples prepared in various Ni/Ce ratios and then heated at 400°C, (a) 10/0, (b) 9/1, (c) 8/2, (d) 5/5, (e) 2/8, and (f) 0/10.

heated at 400°C. The main part of particle of sample prepared in Ni/Ce=10/0 was from 100 to 10 µm in size. The cerium substituted samples had smaller particle size than sample prepared in Ni/Ce=10/0. In contrast, sample prepared in Ni/Ce=0/10 had much larger particles. Particle size distribution of samples prepared in this work was less affected from heating temperature. As an exception, sample prepared in Ni/Ce=0/10 without heating had smaller particles than 100 µm in size.

TABLE 2 shows the specific surface area of samples synthesized in various Ni/Ce ratios. Specific surface area and particle size has influence on color, and solubility of phosphate materials. Specific surface area of nickel phosphate increased by the substitution with cerium. Samples prepared in all Ni/Ce ratios had smaller specific surface area by heating.

PIGMENTAL PROPERTIES OF PHOSPHATES

The color of samples without heating changed from light green to white with the increase of cerium ratio. By heating, light green of nickel hydrogenphosphate transformed to dark yellow powder of nickel pyrophosphate. FIGURE 6 shows UV-Vis reflectance spectra of samples synthesized in various Ni/Ce ratios and then heated at 400°C. Sample in Ni/Ce=10/0 had strong reflectance at 340 and 660 nm. In contrast, the reflectance at 440 nm was weak. The light at 660 and 440 nm was orange and dark blue in color, respectively. Therefore, this sample seemed orange-colored powder. These characteristic points became weak with the increase
FIGURE 6 UV-Vis reflectance spectra of samples prepared in various Ni/Ce ratios and then heated at 400°C, (a) 10/0, (b) 9/1, (c) 8/2, (d) 5/5, (e) 2/8, and (f) 0/10.

FIGURE 7 Acid resistance of samples heated at 400°C, (a) nickel, (b) cerium, and (c) phosphorus.

of cerium ratio. Samples lost the color by the addition of cerium.

FIGURE 7 shows acid resistance of samples synthesized in various Ni/Ce ratios and then heated at 400°C. The small number of solubility means high acid resistance. The eluted ratio of phosphorus changed from 100 to 19% with the increase of cerium ratio. Formation of cerium phosphate inhibited the elution of phosphate materials. Not only particles consisted of nickel phosphate was obtained, but also the composite particles between nickel phosphate and cerium phosphate were synthesized in these conditions.

In basic solution, all samples indicated no elution of nickel and cerium cations, because of the formation of their hydroxides. TABLE 3 shows the solubility of phosphorus in sodium hydroxide solution. The eluted ratio of phosphorus decreased with the increase of cerium ratio. Samples had high base resistance by heating at high temperature.

<table>
<thead>
<tr>
<th>Ni/Ce</th>
<th>Temperature /°C</th>
<th>R.T.</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/0</td>
<td>87.47</td>
<td>67.96</td>
<td>62.70</td>
<td>46.59</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>9/1</td>
<td>74.47</td>
<td>63.06</td>
<td>44.96</td>
<td>33.68</td>
<td>4.99</td>
<td></td>
</tr>
<tr>
<td>8/2</td>
<td>79.13</td>
<td>67.27</td>
<td>44.34</td>
<td>36.40</td>
<td>4.35</td>
<td></td>
</tr>
<tr>
<td>5/5</td>
<td>45.93</td>
<td>50.35</td>
<td>31.51</td>
<td>20.88</td>
<td>6.17</td>
<td></td>
</tr>
<tr>
<td>2/8</td>
<td>24.89</td>
<td>17.09</td>
<td>13.40</td>
<td>9.44</td>
<td>6.93</td>
<td></td>
</tr>
<tr>
<td>0/10</td>
<td>10.52</td>
<td>9.45</td>
<td>7.90</td>
<td>7.52</td>
<td>7.18</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3 Elution ratio of phosphorus as base resistance of samples /%

CONCLUSIONS

In this work, nickel - cerium phosphates were prepared in aqueous solution. The obtained products were estimated for design of functional materials. The following phenomena were clarified.

1. The cerium ratio in precipitates was higher than that in preparation process.
2. By the substitution of cerium cation, samples changed the mixture of nickel phosphate and cerium phosphate.
3. Nickel phosphate had pillar-like particles. This shape of particles disappeared by the substitution with cerium.
4. Specific surface area of samples increased with the ratio of cerium.
5. The color of nickel phosphate was changed from light green to dark yellow by heating. These colors were whitened by the substitution with cerium.
6. The acid and base resistance of nickel phosphate materials improved with the increase of cerium ratio.

REFERENCES


