Effects of melting temperature on cerium oxidation state and crystallization on catalytic properties in cerium phosphate glasses

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The effect of the melting temperature on the cerium oxidation state and crystallization of cerium phosphate glasses with a molar composition $30\text{CeO}_2\text{--}70\text{P}_2\text{O}_5$ was investigated. Ce^{3+} and Ce^{4+} ion concentration changes in the glass attributable to the melting temperature were investigated by X-ray photoelectron spectroscopy analysis. The crystallization kinetics of the glasses and the activation energy for crystallization were evaluated under non-isothermal conditions using differential thermal analysis (DTA) performed at different heating rates. Each DTA curve exhibited one exothermic peak associated with the crystallization of the glass. The crystalline phase was identified as CePO_4 via X-ray diffractometry analysis. The Kissinger and Marotta methods were used to calculate the local activation energies for the glass samples. The amount of precipitated CePO_4 with heating at 890 K increased as the melting temperature (or Ce^{3+}) increased. The catalytic properties were studied by thermogravimetric analysis, which showed that a greater amount of precipitated CePO_4 led to poorer catalytic properties of the glass.

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1. Introduction

Cerium has a different electronic structure from common metals, as the unfilled 4f orbitals are shielded from interactions with the surrounding environment by a full octet of electrons in the $5s^2p^6$ outer shell. Owing to this electronic structure, cerium oxide has been studied for its reduction behavior and non-stoichiometric^{1),2)} and metal-ceria interactions.^{3),4)} In addition to these studies, cerium has catalytic properties in glasses. The catalytic properties of glasses containing CeO_2 have been studied for the self-cleaning of household ovens^{5),6)} and catalyzed diesel particulate fillers.^{7),8)}

To improve the catalytic properties of glass, the solubility of CeO_2 having catalytic properties must be increased, and the glass must be homogeneous and without phase separation. The solubility of rare-earth ions in glass varies greatly depending on the type of glass.^{9)–11)} Rare-earth ions have a high field strength and thus tend to form clusters.^{9),10)} The solubility of rare-earth ions in pure silicate glass is less than 1 mol %, but phosphate-based glass is capable of dissolving large quantities of rare-earth ions because it suppresses the formation of clusters.¹¹⁾ Thus, phosphate-based glasses are good candidates as hosts for catalytic applications.

The catalytic properties of the catalytic material decrease when CePO_4 precipitates owing to the inhibition of the redox reaction between Ce^{3+} and Ce^{4+} .^{12)–14)} Studies have investigated the decrease in the catalytic properties when CePO_4 is precipitated.¹⁵⁾ However, few studies have been performed for preventing CePO_4 precipitation to improve the catalytic performance.

The concentration of Ce^{3+} and Ce^{4+} ions depends on the melting temperature, time, and atmosphere.^{16)–18)} In this work, we focus on the crystallization kinetics of $\text{CeO}_2\text{--P}_2\text{O}_5$ glass by varying the melting temperature to change the concentration of Ce^{3+} and Ce^{4+} ions for reducing the precipitation of CePO_4 .

2. Experimental procedure

2.1 Glass preparation

A well-mixed batch (~50 g) with a molar composition of $30\text{CeO}_2\text{--}70\text{P}_2\text{O}_5$ was prepared by mixing analytical reagent grades of CeO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$. Alumina crucibles containing the batch were heated at 600°C for ~2 h to evaporate the water and ammonia in the batch and minimize the tendency of subsequent phosphate loss and then taken to another electric furnace preheated from 1,300 to 1,500°C. The batch was held at the temperature for 1 h in air. The molten glass was quenched onto a cold stainless-steel plate. The obtained glasses were not annealed. The glasses were ground and crushed with a 44- μm mesh and kept in a vacuum desiccator to avoid moisture attack.

2.2 Measurements and analysis

The change in the concentration of the Ce^{4+} and Ce^{3+} ions caused by the melting temperature was analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectrum was recorded using an ESCALAB 250 XPS system and a Theta Probe XPS system with monochromatic $\text{AlK}\alpha$ ($h\nu = 1,486.6$ eV) radiation. An analysis area 400 μm in diameter was used and was calibrated with reference to C1s (284.6 eV).

The crystallization kinetics of the glasses were investigated by non-isothermal differential thermal analysis (DTA). The DTA measurements were performed using ~30 mg of the heat-treated glass powders in an air atmosphere with heating to 800°C at rates of 5, 10, 15, and 20°C/min. Model DTG-60H (Shimadzu) and an alumina pan were used. The DTA results were analyzed to determine the crystallization mode and the activation-energy values for the crystallization of each sample using the Kissinger¹⁹⁾ and Marotta methods.²⁰⁾ The slope of each graph was determined using the least-squares method. To identify the crystalline phases formed during the DTA heat treatment, X-ray diffraction (XRD, Rigaku-Ultima IV) were performed.

To study the effect of precipitated CePO_4 on catalytic proper-

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ties, we investigated the temperature at which the fatty acid started to oxidize to CO₂ and the temperature at which oxidation ended. The oxidation of the fatty acid was examined by measuring the weight loss of the sample using thermogravimetric analysis (TGA, Q600SDT, TA Instruments).

The TGA measurements were performed using 0.02 ± 0.005 mg of the glass powders and 0.02 ± 0.005 mg of stearic acid in an atmosphere of N₂ gas, with heating to 400°C at rates of 10°C/min.

3. Results and discussion

3.1 Effect of melting conditions on cerium oxidation state

The Ce 3*d* XPS spectra of 30CeO₂–70P₂O₅ obtained under different melting conditions are presented in **Fig. 1**. We followed the work of Eric et al.²¹⁾ for distinguishing the Ce³⁺ peaks from the Ce⁴⁺ peaks. Ce³⁺ peaks appeared at *v*⁰ (880.9 eV), *v*[′] (885.2 eV), *u*⁰ (899.1 eV), and *u*[′] (903.4 eV), and Ce⁴⁺ peaks appeared at *v* (882.7 eV), *v*^{′′} (888.5 eV), *v*^{′′′} (893.3 eV), *u* (901.3 eV), *u*^{′′} (907.3 eV), and *u*^{′′′} (916.9 eV).²¹⁾ The *u*^{′′′} peak area shown in **Fig. 1** that hardly overlaps with other peaks was reduced, and it

Fig. 1. Ce 3*d* core level peak for the glass melting condition curve fitted with eight individual peaks corresponding to contributions from Ce³⁺ and Ce⁴⁺ ions. [(a): 1,300°C, 1 h melting; (b): 1,400°C, 1 h melting; (c): 1,500°C, 1 h melting], [··· line: Ce⁴⁺, --- line: Ce³⁺].

can be qualitatively confirmed that the concentration of Ce³⁺ ions decreased as the melting temperature decreased. The concentrations of Ce³⁺ and Ce⁴⁺ ions were calculated using the Gauss method within an error of ± 0.3 eV from each peak in the Ce 3*d* spectra and are presented in the **Table 1**.

Figure 1 shows the equilibrium Ce³⁺ and Ce⁴⁺ ions. The equilibrium state of the Ce ions was affected by the melting temperature. From a theoretical viewpoint, the sign of the standard enthalpy of the Ce₂O₃–CeO₂ oxidation reaction in the Ellingham diagram is positive ($\Delta H^0 < 0$). Therefore, this oxidation reaction is exothermic, and the slope of the free energy line with respect to the temperature is given as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (1)$$

The oxidation–reduction of the oxide melt is expressed as follows:

The activity of the oxide ions of the liquid phase in a restricted temperature range hardly changes;²²⁾ it is constant depending on the chemical composition. Thus, Eq. (2) is rewritten as follows:

$$4 \log(\text{Ce}^{4+}/\text{Ce}^{3+}) = \log K + \text{constant} \quad (3)$$

According to the Van't Hoff equation,

$$\log K = -\Delta H/(4.575 T) + \text{constant} \quad (4)$$

Combining Eqs. (3) and (4) yields

$$4 \log(\text{Ce}^{4+}/\text{Ce}^{3+}) = -\Delta H/(4.575 T) + \text{constant} \quad (5)$$

In Eq. (5), ΔH is a negative value; i.e., the oxidation state of the Ce ions shifts toward the reduced species as the temperature increases.

3.2 Thermal and structural characterization

DTA curves measured at 15 K/min in N₂ for glasses obtained with different melting temperatures are shown in **Fig. 2**. As shown

Table 1. Ce³⁺ and Ce⁴⁺ ion concentrations in CeO₂–P₂O₅ glasses for the following melting conditions

Melting conditions	Ce (III)	Ce (IV)
1300°C 1 h	56.4%	43.6%
1400°C 1 h	60.1%	39.9%
1500°C 1 h	63.4%	36.6%

Fig. 2. DTA curves for the glass powder obtained at different melting temperatures with a heating rate of 15 K/min.

Fig. 3. XRD patterns of glass samples heat-treated at various temperatures.

in Fig. 2, each glass powder had one maximum crystallization temperature peak, T_p . The software used for exothermal peak fitting was Origin Pro 8.²¹⁾ The T_g peak decreases with increasing concentration of Ce^{3+} . The T_g peak change is thought to be that Ce–O bond length and coordination number are longer and larger for Ce^{3+} than Ce^{4+} .⁹⁾ The T_p peak for the glasses moved to lower temperatures when melting temperature increased, i.e., when concentration of Ce^{3+} ions in the glass increased.

XRD analysis was performed to confirm nucleation during DTA. **Figure 3** presents the XRD patterns for the glass samples heated at 15 K/min from room temperature to the indicated temperature and maintained at each temperature for 2 h. These results show that no crystallization occurred for the samples heated at 800°C ($T_g < T < T_c$ for all DTA heating rates), whereas the samples heated at a temperature higher than T_c for 1 h exhibited diffraction peaks. The XRD results in Fig. 3 indicate that the exothermic peaks in the DTA curves are associated with the crystalline phase of $CePO_4$.

3.3 Kinetic parameters of crystal growth

The activation energy for crystallization was determined using the Kissinger and Marotta equations:

$$\ln\left(\frac{\alpha}{T_p^2}\right) = -\frac{E_c}{RT_p} + \text{constant}, \quad (6)$$

$$\ln \alpha = -\frac{E_c}{RT_p} + \text{constant}, \quad (7)$$

where α is the DTA heating rate, E_c is the activation energy, T_p is the maximum crystallization temperature, and R is the gas constant.

The $\ln(T_p^2/\alpha)$ vs. $1/T_p$ [Eq. (6)] and $\ln(\alpha)$ vs. $1/T_p$ [Eq. (7)] plots for the glasses melted at different temperatures obtained at heating rates (α) of 5, 10, 15, and 20 K/min are shown in **Fig. 4**. The activation energy for crystallization, E_c , determined according to the slope of these straight lines is given in **Table 2**.

The activation energies obtained according to Eqs. (6) and (7) were 338 and 352 KJ/mol, respectively, for the glass melted at the 1,300°C exothermic peak. The activation energies of the glass melted at 1,400°C were 304 and 318 KJ/mol, and those of the glass melted at 1,500°C were 278 and 292 KJ/mol. For both the Kissinger and Marotta equations, the activation energy of crystallization decreased when the melting temperature increased. These results suggest that a larger amount of Ce^{3+} ions yields more sites for nucleation, and the crystallization tendency increases with the increasing concentration of Ce^{3+} ions.

Fig. 4. Kissinger and Marotta plots for the crystallization peaks.

Table 2. Thermal properties as measured by DTA at a heating rate of 15 K/min in a nitrogen atmosphere for the crystallization peaks of glasses formed by melting at different temperatures for 1 h in air

Sample	Melting temp. (°C)	T_g (K)	T_c (K)	T_p (K)	Kissinger-activation energy E_c (kJ/mol)	Marotta-activation energy E_c (kJ/mol)
A	1300	772	864	890	338	352
B	1400	768	857	886	304	318
C	1500	766	851	883	278	292

3.4 Catalytic properties

Fatty acid was lost the weight by the oxidation reaction with the converted into a gas.²³⁾ The catalyst promotes the oxidation by reducing the oxidation temperature of the fatty acid. We compared the performance of a glass catalyst subjected to by weight loss due to oxidation.

The TGA results for stearic acid and glass samples heated at different conditions are shown in **Fig. 5** and **Table 3**. The

Fig. 5. TGA curves for $\text{CeO}_2\text{-P}_2\text{O}_5$ glass catalysts in stearic acid mixed at a weight ratio of approximately 1:1.

Table 3. Weight loss of stearic acid with $\text{CeO}_2\text{-P}_2\text{O}_5$ glasses formed by melting at different temperatures for 1 h in air and heating at different conditions

Sample	Melting temp. (°C)	Heating conditions	Start temp. of weight loss (°C)	Finish temp. of weight loss (°C)
A	1300	—	236.7	289.2
B	1300	890 K 1 h	244.3	296.3
C	1400	890 K 1 h	246.2	299.8
D	1500	890 K 1 h	248.6	304.0

samples were glass frit mixed with stearic acid at a weight ratio of 1:1. For the glass melted at 1,300°C (no CePO_4 precipitated), the starting decomposition temperature was 236.7°C, and the ending decomposition temperature 289.2°C. For the glass melted at different temperatures and heated at 890 K for 1 h (CePO_4 precipitated), the starting decomposition temperatures were 244.3–248.6°C, and the ending decomposition temperature 296.2–304.0°C, as shown Table 3. The temperature at which the stearic acid started to oxidize to CO_2 and the temperature at which the oxidation ended increased with increasing amounts of precipitated CePO_4 .

The reason for the temperature change is thought to be that the redox reaction is inhibited between Ce^{3+} and Ce^{4+} when CePO_4 is precipitated in cerium-based catalysts.^{12)–14)} Hence, as the melting temperature (Ce^{3+}) increases, the precipitation of CePO_4 increases, and the starting temperature of the oxidation of stearic acid and the oxidation ending temperature increase.

4. Conclusion

We investigated the effect of the melting temperature on cerium oxidation state and the effect of the crystallization of cerium phosphate glass on the catalytic properties to further the development of cerium phosphate glass.

The effects of the melting temperature on the cerium oxidation state were studied by XPS. A $30\text{CeO}_2\text{-}70\text{P}_2\text{O}_5$ mol % composition that initially contained only Ce^{4+} ions resulted in glasses that contained both Ce^{3+} and Ce^{4+} ions and increased concentrations of Ce^{3+} when melted at high temperatures.

The crystallization kinetics was studied by non-isothermal

DTA and XRD. The calculated values for glasses melted at 1,300, 1,400, and 1,500°C were 338, 304, and 278 kJ/mol, respectively, according to the Kissinger method and 352, 318, and 292 kJ/mol, respectively, according to the Marotta method.

The catalytic properties were studied by TGA. As the melting temperature (Ce^{3+} ion concentration) increased, the amount of the precipitated CePO_4 crystalline phase increased. A larger amount of precipitated CePO_4 yielded a greater reduction in the catalytic properties of the glass.

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