Crystallization mechanism and catalytic properties with amount of the precipitated CePO₄ for cerium phosphate glass catalyst

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The crystallization kinetics and catalytic properties with amount of precipitated CePO₄ for a 60P₂O₅–9B₂O₃–24ZnO–7CeO₂ glass was investigated. The kinetic parameters, activation energy for crystallization (Eₐ), and Avrami constant (n) were evaluated under non-isothermal conditions using different thermal analysis (DTA) performed at different heating rates. The DTA curves exhibited two overlapping exothermic peaks associated with the crystallization of the glass. BPO₄ was the first crystalline phase to be formed, and it was followed by the formation of CePO₄ as identified by XRD. The calculated values of the local activation energies for the growth of CePO₄ were 452 kJ mol⁻¹, obtained by the Kissinger method, and 464 kJ mol⁻¹, obtained by the Marotta method. The Avrami constants of BPO₄ and CePO₄ were 1.83–2.56 and 1.40–1.54, respectively. The catalytic properties with the amount of precipitated CePO₄ were studied by thermogravimetric analysis (TGA), which showed that the greater the amount of CePO₄ precipitated, the more the catalytic properties of the glass decreased.

Key-words : Crystallization kinetics, DTA, CePO₄, Catalytic property, TGA

1. Introduction

Among the rare earth oxides, which have excellent catalytic ability and high optical properties, cerium oxide in particular has been studied extensively for its reduction behavior and non-stoichiometry, oxygen storage capacity, and metal–ceria interactions. Cerium oxide is also used in phosphate-based glasses. Because these types of glasses are capable of containing large amounts of CeO₂ as compared to silicate-based glasses, the characteristics of cerium oxide in these glasses have actively been studied.

In the study of these cerium phosphate-based glasses, analysis of the structural and optical properties are prevalent; however, studies of the catalytic properties, which are very important properties of cerium oxides, are very limited. In order to study the catalytic properties of cerium phosphate glasses, previous research related to the crystallization is very important. This is because recent studies have reported that when CePO₄ forms in a catalytic material, the redox reaction between Ce³⁺ and Ce⁴⁺, which is the main factor for the catalytic expression of CeO₂, is inhibited, and thus the catalytic properties of the catalyst decrease. Among the studies related to the crystallization of cerium phosphate glasses, precipitation of CePO₄ by heat treating the cerium phosphate glass has been demonstrated. However, the crystallization mechanism, which plays an important role in maximizing the desired catalytic performance, has not been widely studied. Further, very few studies have investigated whether changes in the catalytic properties occur when CePO₄ is precipitated.

In the present work, we focus our attention on the crystallization kinetics of CeO₂–ZnO–B₂O₃–P₂O₅ glass that is the most close composition to the practical use because of it’s chemical stability. Also, we precipitated CePO₄ on the glass by heat processing and confirmed the decrease of catalytic properties for the glass.

2. Experimental procedures

2.1 Glass preparation

Glass with the composition 60P₂O₅–9B₂O₃–24ZnO–7CeO₂ (wt %) was used. Glass samples were prepared using NH₄H₂PO₄, B₂O₃, ZnO, and CeO₂, all of which had purities higher than 99.9%. This mixture was melted in an alumina crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of 850°C for approximately 30 min in order to evaporate ammonia, carbonate, and water from the batch and to minimize the tendency for subsequent phosphate volatilization. The temperature was then increased gradually to 1350°C and maintained at that temperature for 90 min to homogenize the melt. The melt was quenched by pouring it on a plate. The as-quenched glass was ground and screened with a 44 mesh and stored in an oven at 100°C to prevent the introduction of moisture until it was required for the DTA measurements using a model Q600 SDT (TA Instruments).

2.2 Measurements and analysis

Crystallization analysis was performed by a non-isothermal method that is easier and faster than the isothermal method. In order to determine the kinetic parameters of the sample, DTA measurements were performed using approximately 30 mg of the heat-treated glass powders in an air atmosphere at heating rates of 5, 10, 15, and 20°C/min up to 800°C. The DTA results were further analyzed to obtain the crystallization mode and the activation energy values for the crystallization of each sample using the Kissinger, Marotta, and Ozawa methods. The slope of each graph was determined by the method of least squares.

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The phase analysis and crystallization of the heated samples were examined by X-ray diffraction (XRD, Rigaku-Ultima IV) and scanning electron microscopy (SEM, Jeol JSM-5400, Japan). SEM observations were carried out on polished surfaces (mirror finished) that were etched by immersion in a 2 vol% HF solution for 2 s.22)

To study the catalytic properties of the glass, CePO₄ was precipitated, we analyzed the temperature at which the fatty acid started to oxidize to CO₂ and the temperature at which oxidation ended.12),13) A study of the oxidation of the fatty acid was carried out by measuring the weight loss of the sample using thermogravimetric analysis (TGA, Q600SDT, TA Instruments). The fatty acid, palmitic acid and stearic acid (Sigma-Aldrich Co.) were used. TGA measurement conditions were as follows: a 30 mg sample (15 mg of heated glass and 15 mg of fatty acid) was placed in the crucible and heated (heating rate of 10°C/min up to 400°C) with two different gas mixtures (air or 5 vol% of O₂ in N₂).

3. Results and discussion

3.1 Thermal and structural characterization

The DTA curves for the glass powder obtained at different heating rates are presented in Fig. 1. The DTA curves show a first exothermic effect followed by a strong exothermic peak, which are partially overlapped. Figure 2 shows the crystallization exotherms for the DTA curve obtained at a heating rate (α) of 5K/min together with an inset where the separation of the two overlapping crystallization peaks is illustrated. The software used for exotherm peak fitting was OriginPro 8.22) Modeling of the experimental DTA curve was carried out using two partially overlapping Gaussian curves. The characteristic temperatures of the glass (Tg, Tc, Tp) increased with the increase in heating rate, as shown in Table 1. To confirm the nucleation results of the DTA curves, XRD analysis was performed. Figure 3 presents the XRD patterns for the glass samples heated at 10 K/min from room temperature to the indicated temperature and held at each temperature for 1 h. These results show that no crystallization is observed for samples heated at 813 and 853 K (Tg < T < Tc for all α), whereas the samples heated at a temperatures higher than 893 K for 1 h show diffraction peaks. Through Fig. 3 we can confirm that the two exothermic peaks in the DTA curves are the result of crystal phases BPO₄ (peak 1) and CePO₄ (peak 2), respectively.

3.2 Kinetic parameters of crystal growth

The Kissinger and Marotta equations were used to determine the activation energy.

\[
\ln \left( \frac{\alpha}{T_p^2} \right) = - \frac{E_c}{RT_p} + \text{constant} \\
\ln \alpha = - \frac{E_c}{RT_p} + \text{constant} 
\]

where α is the DTA heating rate, Tp the crystallization peak temperature, E_c the activation energy, and R the universal gas constant (8.3144 J mole⁻¹K⁻¹).

The Kissinger and Marotta plots according to Eqs. (1) and (2) for the glass at heating rates of 5, 10, 15, and 20 K/min are shown in Fig. 2. DTA curve obtained at α = 5 K/min. The inset depicts the separation of the overlapped crystallization peaks in the crystallization exotherm.

![Fig. 1. DTA curves for the glass powder obtained at different heating rates.](image)

![Fig. 2. DTA curve obtained at α = 5 K/min. The inset depicts the separation of the overlapped crystallization peaks in the crystallization exotherm.](image)

![Fig. 3. XRD patterns of the glass samples heat-treated at various temperatures.](image)
shown in Fig. 4. The activation energies obtained from the slopes of Fig. 4 are shown in Table 2. It is noted that the values of $E_c$ obtained from Kissinger and Marotta equations are close to each other suggesting the validity of both approaches.

There are several methods for calculating the Avrami constant, $n$, from the activation energy, but in the present study, the Ozawa equation\(^{26,27}\) was used.

$$\left. \frac{d \ln[-\ln(1-x)]}{d \ln \alpha} \right|_T = -n$$

where $x$ is the volume fraction crystallized at a fixed temperature $T$ when heated at $\alpha$.

The value of $x$ at a specific temperature can be determined from the DTA curves\(^{28-30}\) by the ratio $A_T/A$, where $A$ is the total area of the crystallization peak between temperature $T_i$ (where crystallization just begins) and temperature $T_f$ (where the crystallization is completed) and $A_T$ is the area between $T_i$ and $T_f$, as shown schematically in Fig. 5. The graphical representation of $x$ as a function of $T$ for both exothermic peaks shows typical sigmoid curves for different heating rates, as presented in Figs. 6(A) and 6(B), indicating that the formation of the crystalline phase proceeds by a combination of nucleation and growth processes.

The values of $n$, obtained from the slope of Fig. 7, are 1.83 and 2.56 (mean value $\bar{n} = 2.20$) for the first crystallization peak, corresponding to boron phosphate, $\text{BPO}_4$, and 1.40 and 1.54 (mean value $\bar{n} = 1.47$) for the second crystallization peak, corresponding to monazite, $\text{CePO}_4$. Also, we determined that the
The crystallization mechanism of the BPO₄ phase is two-dimensional growth, whereas that of the CePO₄ phase is one-dimensional growth, as shown in Table 3.

3.3 Catalytic properties

If fatty acids are exposed to heat, oxidation reaction of the following occurs:

\[
C_{x}H_{y}O_{2} + zH_{2}O \rightarrow aCO_{2} + bH_{2}O
\]

The catalyst promotes the oxidation by reducing the oxidation temperature of the fatty acid. In this study, catalytic properties were evaluated by weight loss due to oxidation.

Figure 8 shows SEM micrographs of the glass samples after the heating process. We were able to confirm that the longer a sample was maintained at \( T_p \), 933 K, the greater the amount of precipitated CePO₄ crystalline phase.

The TGA results measured by fatty acid and glass samples heated under different conditions are shown in Figs. 9 and 10. The fatty acid and glass samples heated under each condition were mixed at a ratio of 1:1 (wt%). It can be observed that the temperature at which the stearic acid and palmitic acid started to oxidize to CO₂ and the temperature at which oxidation ended increased as a whole with increasing amounts of precipitated CePO₄. Furthermore, from the slope of Figs. 9 and 10, it can be confirmed that the greater the amount of CePO₄ precipitated, the slower the decomposition of the fatty acid. From these results, we can confirm that catalytic properties are reduced when CePO₄ is precipitated, not only in the typical catalytic material but also on the glass. The reason is thought to be that the redox reaction between Ce³⁺ and Ce⁴⁺ is limited when CePO₄ is precipitated, as is the case with other cerium-based catalysts.

![Plot of ln (−ln(1−x)) vs. ln(α) for the two crystallization peaks at two different temperatures.](image)

![SEM photographs of glass samples heated under different conditions: crystallized at 933 K for (A) 30 min and (B) 60 min.](image)

![TGA profiles of glass samples heated under different conditions mixed 1:1 (wt%) with stearic acid: (A) not heated, (B) heated at 933 K for 30 min, and (C) heated at 933 K for 60 min.](image)

![Table 3. Values of \( n \) for different crystallization mechanisms in the heating process](image)
The purpose of this study was to analyze the crystallization mechanism and catalytic properties as a function of the amount of precipitated CePO₄ for the development of cerium phosphate glass having catalytic functionality. The crystallization kinetics of a P₂O₅ – B₂O₃–ZnO–CeO₂ glass were studied by non-isothermal DTA and XRD. The DTA curves exhibited a well-defined crystallization exothermal effect that was formed by the overlapping of two exothermic crystallization peaks. The identification of the crystalline phases by XRD revealed the presence of BPO₄ and CePO₄.

The calculated values of the local activation energies for the growth of BPO₄ were 663 kJ mol⁻¹, obtained by the Kissinger method, and 669 kJ mol⁻¹, obtained by the Marotta method. The calculated values of the local activation energies for the growth of CePO₄ were 452 kJ mol⁻¹, obtained by the Kissinger method, and 464 kJ mol⁻¹, obtained by the Marotta method. The Avrami constants, n, of BPO₄ and CePO₄ were 1.83–2.56 and 1.40–1.53, respectively. The expected crystallization mechanism of the BPO₄ phase is two-dimensional growth and that of CePO₄ is one-dimensional growth.

The catalytic properties as a function of the amount of precipitated CePO₄ were studied by TGA. It was confirmed that the greater the amount of CePO₄ precipitated, the greater the reduction in the catalytic properties of the glass.

Through this study, we have confirmed that in the development of catalytic glass, inhibition of CePO₄ crystal formation is a very important factor. It is expected that the influence of the crystal phase and the crystallization mechanism which were considered in this study, are usefully employed in developing catalytic glasses.

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