Characterization and catalytic behavior of cerium oxide doped into aluminosilicophosphate glasses

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Cerium oxide is commonly used as a catalyst for the oxidation of carbon monoxide (CO) in vehicle exhaust gases, and it is used as a petroleum-cracking catalyst in oil refineries. In this study, cerium aluminosilicophosphate glasses were synthesized and various physical and catalytic properties were measured, including optical properties and decomposition temperatures, by thermogravimetric analysis (TGA) and Fourier transform infrared (FT-IR) analysis. Ce$^{3+}$/Ce$^{4+}$ ratios and structural changes in the glass attributable to doping with ~25 mol% CeO$_2$ were investigated by FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis. Changes in the catalytic properties of the glasses as a function of CeO$_2$ content were confirmed by changes in the decomposition starting temperatures. These temperatures decreased with increasing CeO$_2$ content of the glasses. We also discuss the role of CeO$_2$ in terms of the catalytic properties of the glass structure.

1. Introduction

Cerium oxide is a catalyst with a high oxygen-storage capacity, high surface reactivity, and phase-change desorption capability. Also, cerium has a unique electronic structure, in which the unfulfilled 4f orbitals are shielded from interactions with the surrounding environment by a full octet of electrons in the 5s$^2$p$^6$ outer shell. Because of this unique electronic structure, cerium oxide has been used in non-stoichiometric$^{[1,2]}$ and oxygen storage applications$^{[3-5]}$ and metal–ceria interactions$^{[6,7]}$. It has also been used to enhance hydrophobicity.$^9$

In general, CeO$_2$ becomes many amount is added to the phosphate system in the glass than the addition has been silicate-based glass in the formula oxide in the glass, CeO$_2$ phosphate-based glass that has been the addition is, the majority crystallization it occurred, the ratio between these two species changes. If precipitation occurs, the effectiveness of the catalyst is reduced and the deformation of the molecular structure. The relationship between precipitation and degree of ionic bonding and electronegativity was studied in terms of the catalytic reaction.

Therefore, cerium oxide-doped aluminosilicophosphate (SAP) glasses were synthesized and characterized. The addition of CeO$_2$ was expected to cross-link the glass network and increase the catalytic properties for the fatty acid (stearic acid).

2. Experimental procedure

2.1 Preparation of glass samples

Glasses with compositions of 15 SiO$_2$–15 Al$_2$O$_3$–70 P$_2$O$_5$–(0 + x) CeO$_2$ (x = 0–25 mol%) were prepared (see Table 1). The glasses were prepared from reagent grade SiO$_2$, Al$_2$O$_3$, NH$_4$H$_2$PO$_4$, and CeO$_2$. Well-mixed batches calculated to yield 50 g of glass were melted in a clay crucible for 0.5 h at 1500°C. The glass melt was quenched by pouring it on a stainless steel filter. The obtained glasses were annealed at their glass-transition temperatures ($T_g$) for 2 h and then cut and mechanically polished to obtain samples for thermal and chemical analysis. We also created pellets made of SAP and SAPC glass frit (20 g). The pellets were fired at 1000°C for 5 min. To record the infrared (IR) absorption spectra of the glass samples, the KBr pellet technique was employed. The glass samples were ground to a fine powder.

| Table 1. Analyzed compositions of SAP and SAPC glasses |
|-----------------|-----------------|-----------------|-----------------|
| Glass           | SiO$_2$ (%)     | Al$_2$O$_3$ (%) | P$_2$O$_5$ (%)  | CeO$_2$ (%)    |
| SAP             | 15.00           | 15.00           | 70.00           | 0.00           |
| SAPC1           | 15.00           | 15.00           | 70.00           | 5.00           |
| SAPC2           | 15.00           | 15.00           | 70.00           | 10.00          |
| SAPC3           | 15.00           | 15.00           | 70.00           | 15.00          |
| SAPC4           | 15.00           | 15.00           | 70.00           | 20.00          |
| SAPC5           | 15.00           | 15.00           | 70.00           | 25.00          |

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and a weighed quantity (0.001 g) of the powder was thoroughly mixed with desiccated, highly purified (99.99%) KBr powder (0.1 g). The mixtures were pressed into thin pellets to record the spectra.

2.2 Measurements

The thermal behavior of the glasses was examined with differential thermal analysis (DTA) (TA, Q600) operating in the temperature range 298–1473 K using a heating rate of 10 K/min. The structures of the glasses were analyzed by Fourier transform infrared (FT-IR) spectroscopy (Spectrum GX). We performed thermogravimetric analysis (TGA) (TA, Q600) measurements using 0.01 ± 0.005 mg of the glass powders and 0.01 ± 0.005 mg of a fatty acid (stearic acid) under an atmosphere of N2 gas and using heating rates of 10°C/min up to 500°C. We also checked the type of the upper analyzed by X-ray diffraction (XRD) (Ringaku X-ray diffractometer, Cu Kα, 30 kV, 20 mA). X-ray photoelectron spectroscopy (XPS) measurements were taken using the ESCALAB 250 XPS system and Theta Probe XPS system using monochromatic AlKα (hν = 1486.6 eV) radiation conditions. An analysis area of 400 μm in diameter was used and it was corrected to reference C1s (284.6 eV).

3. Results and discussion

3.1 DTA & XRD analysis

Among the studies related to the crystallization of cerium phosphate glasses, precipitation of CePO4 by heat treating the cerium phosphate glass has been demonstrated. Therefore, we checked for the formation CePO4 in the SAP and SAPC glasses. The DTA and XRD results are shown in Fig. 1.

The DTA curves do not show an onset crystallization temperature (Tc), and peak crystallization temperatures (Tp) and appear broad peak in XRD data. Thus, we considered there was no crystallization of CePO4 on the SAP and SAPC glasses.

3.2 TGA analysis

We compared the performance of the glass catalyst with that of CeO2, which has been reported to be a very good oxidation catalyst. The TGA curve for the mixture of the glass frit and stearic acid in a weight ratio of 1:1 are shown in Fig. 2. For SAP glass frit and SAPC glass frit + stearic acid, the starting decomposition temperatures were 233–270°C and the closing decomposition temperatures were 285–322°C, as shown in Table 2.

These points can be guessed by the following reaction mechanism. At decomposition temperature the Ce atoms of glass frit interface are mostly covered by COads. These COads do not dispose of any atomic oxygen on glass frit but they are able to pick up the “oxide” oxygen atoms provided by the interfacial ceria as already demonstrated in work. Thus, we think that the first stage of the reaction consists of the formation of CO2 via the reduction of the interfacial ceria by carbon monoxide adsorbed on glass frit. The CO2 desorption leads to vacant site on the interfacial glass frit and makes possible the dissociative adsorption of stearic acid. Ceria is then regenerated by a spill-over phenomenon of Oads toward Ce2O3 and re-oxidation of the interface into CeO2. This interpretation is described by the following three steps:

\[ \text{COads} + 2\text{CeO}_2 \rightarrow \text{CO}_2 + ^* + \text{Ce}_2\text{O}_3 \]  \hspace{1cm} (1)

\[ 1/2\text{O}_2 + ^* \rightarrow \text{Oads} \]  \hspace{1cm} (2)

\[ \text{Oads} + \text{Ce}_2\text{O}_3 \rightarrow 2\text{CeO}_2 + ^* \]  \hspace{1cm} (3)

where the asterisk (*) stands for an adsorption site on glass frit and “ads” indicates an adsorbed species.

From this mechanism, the very high activity observed for the pre-reduced glass–CeO2 catalyst would be the possibility of initiating the CO oxidation without any vacant sites for the dissociation of oxygen.

According to Yusaku et al., isobutene is adsorbed onto the lattice O²⁻ and Ce⁴⁺ to form isobuthylcarbenium ions and H⁺. Isobutene is released from butylcarbenium, leaving one proton. The electron of H migrates to Ce⁴⁺ to form Ce⁵⁺ and H radical. The elimination of a water molecule from the surface results in the formation of OH and H radicals to form a pair of Ce⁵⁺ ions.

Fig. 1. DTA curves of glasses from the SiO2-Al2O3-P2O5-CeO2 system. The inset shows the XRD curve of SAPC5 glass at 1000°C for 30 min.

![Fig. 1. DTA curves of glasses from the SiO2-Al2O3-P2O5-CeO2 system. The inset shows the XRD curve of SAPC5 glass at 1000°C for 30 min.](image)

![Fig. 2. TGA curves for SAP and SAPC glass catalysts in stearic acid mixed in weight ratios of approximately 1:1.](image)

| Table 2. Starting and closing decomposition temperatures for SAP and SAPC glass catalysts mixed with stearic acid |
|---------------------------------------------------------------|
| **Starting Stearic Acid Decomposition Temperature (°C)** & **Closing Stearic Acid Decomposition Temperature (°C)** |
| **Temperature (°C)** | ** Starting Decomposition Temperature** | ** Closing Decomposition Temperature** |
|-------------------|-------------------------------|-------------------------------------|
| SAP               | 270.19                        | 322.16                              |
| SAPC1             | 249.23                        | 301.12                              |
| SAPC2             | 244.25                        | 296.23                              |
| SAPC3             | 240.25                        | 292.22                              |
| SAPC4             | 236.01                        | 287.99                              |
| SAPC5             | 233.02                        | 284.99                              |
which is then oxidized by molecular oxygen to Ce$^{4+}$, i.e., its original state.\textsuperscript{22} That is why SAPC glasses performed well in comparison to another developmental catalyst. Catalytic property of glass samples was further analyzed by DSC. Through Fig. 3, it is confirmed that change of the endothermic peak of glass samples is similar to the results of TGA. The explanation of these results was confirmed through a structural analysis.

3.3 UV–vis spectroscopy

Figure 4 shows the optical absorption spectra of the SAP and SAPC glasses. It was observed that the band edge of the glasses progressively shifted toward longer wavelengths in the region from 320 to 420 nm. It shifted more from approximately 325 to 345 nm. The influence of irradiation is explained by the following reaction:

$$\text{Ce}^{3+} + \text{HC} \rightarrow \text{Ce}^{4+} / \text{Ce}^{4+} + \text{EC} \rightarrow \text{Ce}^{3+}.$$

where HC is the hole center captured by the cations and EC is the electron center captured by the anions.\textsuperscript{23–25}

The continuous shifting of the band edge in these glasses confirms that the Ce$^{3+} + \text{HC} \rightarrow \text{Ce}^{4+}$ reaction is the predominant reaction. It was also observed that the irradiation-induced absorption band from 320 to 420 nm extended to longer wavelengths, which is due to the origin of Ce$^{4+}$ ions.

The optical band gap of the samples after irradiation was obtained by using the plot between $(\alpha h \nu)^{1/2}$ and energy ($h \nu$), where $\alpha$, $h$, and $\nu$ are the absorption coefficient, Planck’s constant, and frequency, respectively.\textsuperscript{26} The values of the optical energy gap were obtained from the line on the plot shown in Fig. 5. The optical band-gap energy shifts to a lower energy with the change in composition. This is due to the formation of more tetrahedral [PO$_4$] groups and Ce$^{4+}$ ions in the glasses. It is observed that with the addition of CeO$_2$, a large number of oxygen ions are available in the glass network by breaking up the P–O–P linkages in the Q$_2$ unit, creating non-bridging oxygen (NBO) atoms by forming ionic bonds.

As reported in the literature, forming NBOs in glass networks affects the structural and optical behavior of the glass. The oxygen atoms are utilized by cerium oxide for converting the Ce$^{3+}$ groups to Ce$^{4+}$ groups. These factors shift the absorption edge to the lower energy, which leads to a significant compaction in the band gap (shown in Fig. 5). This change in band gap shows that the CeO$_2$ acts as a network modifier.

3.4 FT-IR analysis

The FT-IR transmission spectra recorded for the SAP and SAPC glasses is shown in Fig. 6. We examined the FT-IR spectra to determine the influence of non-crosslinked oxygen on the catalytic properties of the glasses. In the glasses fabricated in the current study, the introduction of aluminum is generally considered to play the role of a former
rather than a modifier. Aluminum and silicon have similar masses and ionic ratios, which favor coupling of their vibrations. The band at approximately 540 cm$^{-1}$ is attributed to the bending vibration of O–P–O and the next peak located at approximately 680 cm$^{-1}$ is attributed to the symmetric stretching of the P–O–P mode vibration in the long-chain phosphate groups (Q$_2$ unit). The peak at 740 cm$^{-1}$ is attributed to the symmetric stretching of the P–O–P mode (Q$_0$ unit). Also, the band at approximately 1150 cm$^{-1}$ is attributed to the symmetric stretching mode of the O–P–O non-bridging oxygen, indicating the formation of a Q$_2$ phosphate tetrahedral. With the increase of CeO$_2$ content, the intensity of the O–P–O bending vibration increases. Higher CeO$_2$ content leads to bonds that are shorter than the phosphate ionic bonds. At the same time, CeO$_2$ ions enter the glass network by breaking up the P–O–P linkages in Q$_2$ units, creating NBOs by forming ionic bonds, which decreases the Q$_2$ unit.

When the glasses were doped with 5 mol% of CeO$_2$, the intensity of the band due to [PO$_2$] units was observed to decrease, and correspondence to this a new band is rise at approximately 450 cm$^{-1}$ band. This band is attributed to the presence of a Ce–O stretching vibration. In some cases, it refers to the formation of cerium units combined with the network. The change of band intensity at approximately 450 cm$^{-1}$ with increasing CeO$_2$ content leads one to consider that this band is due more to vibrations of the modifier than to those of the network former CeO$_2$ unit. Furthermore, rare-earth ions were found to play the role of a modifier in aluminophosphate glasses and cation coordination numbers were determined. Also, Du et al. reported that the Ce–P–P–P first-peak intensity is stronger for Ce$^{4+}$ than for Ce$^{3+}$. This is consistent with the higher field strength of Ce$^{4+}$ ions, which would be accompanied by a higher incidence of non-bridging oxygen ions in the first coordination shell. Hence, cerium plays the role of a modifier in phosphate networks. As the CeO$_2$ amount increases, the number of Ce$^{4+}$ ions increases.

### 3.5 XPS analysis

In XPS, the chemical state of an element is manifest in chemical shifts of core-level photoelectron peaks. Here, the ability to distinguish between Ce$^{3+}$ and Ce$^{4+}$ is of primary interest, and in this case, photoelectron peaks associated with core-level transitions in the 3$d$ spectra of Ce possess the relevant information. However, the multitude of overlapping 3$d$ photoelectron transitions for Ce creates a set of peaks whose quantitative analysis requires curve-fitting. We followed the work and notation of Romeo and Pfau, who identified ten peaks (five pairs) in the 3$d$ region, as shown in Fig. 7. Those five peaks, designated as $\nu$ peaks, belong to the 3$d_{3/2}$ spin–orbit split doublet, and the five analogous peaks in the 3$d_{5/2}$ spin–orbit split doublet are designated as $\mu$ peaks. Of these ten peaks, two pairs are assigned to Ce$^{3+}$ ($\mu_0$, $\mu_1$, $\mu_2$, $\mu_3$), whereas the remaining three pairs are assigned to Ce$^{4+}$ ($\nu_0$, $\nu_1$, $\nu_2$, $\nu_3$). These ten peaks overlap into three adjacent regions: the first encompasses four peaks from the 3$d_{3/2}$ spin–orbit split doublet ($\mu_0$, $\mu_1$, $\nu_1$, $\nu_2$), the second encompasses the $\nu_1$ peak and four peaks from the 3$d_{5/2}$ spin–orbit split doublet ($\mu_0$, $\mu_1$, $\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$), and the $\nu_2$ peak stands alone. The abundance of these species is reported in Table 3. It was observed that at low Ce content, the preferred oxidation state is Ce$^{3+}$; however, with increasing Ce content in these glasses, the presence of the Ce$^{4+}$ species gradually increases, a phenomenon also observed by other research groups. Pestirakov et al. reported that the addition of CeO$_2$ and Zr$_2$O$_3$ to Au clusters stabilizes the Au$^{2+}$ (0 < $\delta$ < 1) oxidation state due to electron transfer from gold to the metal oxide.

![Fig. 7. Ce 3$d$ core-level peaks for the (a) $x = 5$, (b) $x = 15$, and (c) $x = 20$ glass composition curve fitted with ten individual peaks corresponding to contributions from Ce(III) ions ($\mu$ line) and Ce(IV) ions ($\nu$ line).](image-url)
The reduction of Ce⁴⁺ to Ce³⁺ after deposition of Au on CeO₂ (1 1 1) was observed by Skoda et al.⁶⁶¹

4. Conclusion

We investigated the effect of CeO₂ content on the catalytic behavior of SiO₂-Al₂O₃-P₂O₅-CeO₂ glasses (SAPC system) by open-crucible melting. Their catalytic properties increased with increasing CeO₂ content. The reasons for the change in the catalytic properties of the SAPC glass samples were investigated through the use of UV-vis/FT-IR/XPS measurements. It was confirmed that CeO₂ acts as a network modifier in aluminosilicate glasses. Also, CeO₂ is present as Ce³⁺ and Ce⁴⁺ in the glass, depending on the percentage of Ce³⁺/Ce⁴⁺, and varying catalytic properties by varying the energy band gap. And show a tendency to increase the greater the amount of Ce⁴⁺ when the catalytic properties, such Ce⁴⁺ ions were able to see trends formed by network modifier in the glass. Therefore, in order to understand the catalytic properties in glass, more catalytic materials need to be studied in terms of changes in the structure of glass. Additional fundamental and applied research needs to be performed in order to design improved or new active glass-based systems for different catalytic applications.

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