

Interaction between ultrafine ceria particles and glycine

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An ultrafine ceria powder of 15 nm equivalent spherical particle diameter was dispersed at 2 vol% solid in aqueous solutions with and without glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) of 0.05-5.0 mass% against ceria. The addition of glycine increased the zeta potential of the ceria toward positive values in acidic suspensions. The phase separation of ceria suspensions due to the decreased repulsive energy with decreasing particle size, was suppressed by the steric stabilization effect of the adsorbed glycine. No significant influence of the glycine addition on the zeta potential and phase separation of the basic suspension was measured.

Key words: Ceria, Glycine, Zeta potential, Phase separation, Dispersibility.

Introduction

Colloidal processing comprises the dispersion of fine ceramic particles in a liquid medium and subsequent consolidation of colloidal particles [1-4]. This process affords a uniform microstructure and high packing density of powder compacts. The dispersibility of the colloidal suspension affects both the sintering behavior and resultant properties of densified ceramics. Dispersants such as polyacrylic acid [5, 6], an ammonium salt of polyacrylic acid [7], polymethacrylic acid [8], ammonium polymethacrylate [9, 10] and phosphate ester [11] are added to prepare a stable suspension with a high content of ceramic powder and suitable viscosity. When the size of the colloidal particles becomes smaller, control of the properties of the colloidal suspension encounters a difficulty due to the increased interparticle interaction. i.e., a high viscosity at a low solid content, low dispersibility of the colloidal particles due to decreased repulsive force and a large amount of dispersant to cover the high specific surface area of colloidal particles [11-16]. One strategy to solve the above problems is to find a low molecular weight dispersant with a strong dispersibility. Our brain storm reached the following criteria to look for a possible dispersant for nanometer-sized particles: (1) the size ratio of polymer dispersant to submicrometer-sized particles in a well-dispersed suspension should be retained for the suspension of nanometer-sized particles (steric stabilization effect) [7, 8, 17] and (2) a dispersant of low molecular weight compared to nanometer-sized particles should be highly charged to give a strong

electrostatic stabilization effect [18, 19]. With these ideas in mind, a high possibility for a dispersant was given to an amino acid with two types of ionizable groups (carboxyl and amino groups). These ionized groups provide two roles: adsorption onto particle surfaces and electrostatic repulsion by another group, depending on the pH of the suspension. In this study, an ultrafine ceria powder was dispersed in aqueous solution with glycine to investigate interactions between them.

Experimental Procedure

Ceria powder

A fine ceria powder was collected by drying a commercial ceria suspension (Nyacol Nano Technologies, Inc., MA, USA) using a rotary evaporator below 100°C . Figure 1(a) shows the infrared spectrum of the as-dried ceria powder. HNO_3 and CH_3COOH in the starting suspension remained on the surface of the dried

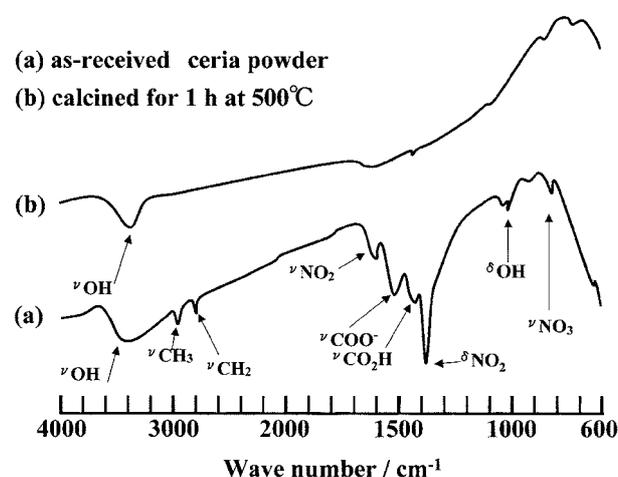


Fig. 1. Infrared spectra of (a) as-dried ceria powder and (b) ceria powder calcined at 500°C .

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Table 1. Heating temperature and specific surface area of ceria powder

Drying or calcination temperature/°C	Specific surface area/m ² ·g ⁻¹	Diameter of equivalent spherical particle/nm
200	111.1	10.4
500	76.6	15.0
600	38.0	30.2
700	0.62	1871

ceria powder. Thermogravimetric-differential thermal analysis (TG-DTA) of the dried ceria powder showed a 9.8% weight loss upon heating to 1000°C. Figure 1(b) shows the infrared spectrum of ceria powder calcined at 500°C for 1 h. The remaining HNO₃ and CH₃COOH in the dried ceria powder disappeared by this calcination. Table 1 indicates the influence of heating temperature on the specific surface area. The specific surface area decreased drastically for the ceria calcined at 700°C. In this experiment, 15 nm-ceria powder calcined at 500°C was used. The zeta potential of the calcined ceria powder was measured as a function of pH at a constant ionic strength of 0.01 M NH₄NO₃ (Rank Mark II, Rank Brothers Ltd., UK).

Dispersant

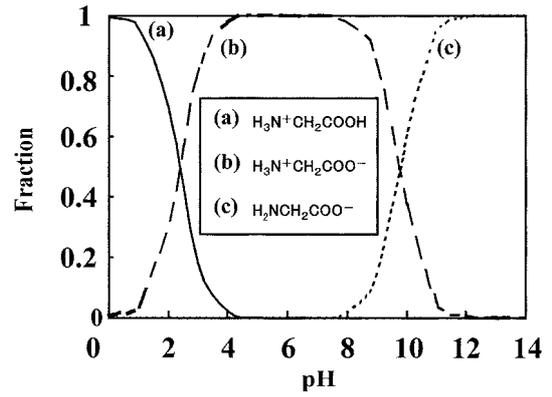
Glycine was used in this experiment as dispersant to the nanometer-sized ceria particles. Table 2 shows the chemical properties of glycine [20]. This amino acid is 0.6 nm in length and provides an 0.04 size ratio to the diameter of the ceria particles. The isoelectric point for equal charge of NH₃⁺ and COO⁻ of glycine is pH 5.97. Figure 2 shows the fraction of dissociated species as a function of pH, calculated using the dissociation constant (Ka) of glycine. The dissociation of glycine (GH) is expressed by Eqs. (1) and (3), and Equations (2) and (4) represent the corresponding equilibrium constants.



$$K_{a1} = \frac{[\text{GH}][\text{H}^+]}{[\text{GH}_2^+]} \quad (2)$$

Table 2. Chemical properties of glycine

Property	Glycine
Chemical formula	H ₂ NCH ₂ COOH
Purity/mass%	99
Molecular weight	75.05
Molecular length/nm	0.6
Isoelectric point	5.97
Solubility	water soluble
Dissociation constant	
pK _{a1}	2.35
pK _{a2}	9.78

**Fig. 2.** Fraction of dissociated glycine as a function of pH.

$$K_{a2} = \frac{[\text{G}^-][\text{H}^+]}{[\text{GH}]} \quad (4)$$

The dissociated fractions of GH₂⁺, GH and G⁻ to the total concentration of neutral and ionized glycine are given by Eqs. (5)-(7).

$$\alpha_{\text{GH}_2^+} = \frac{[\text{GH}_2^+]}{[\text{GH}_2^+] + [\text{GH}] + [\text{G}^-]} \quad (5)$$

$$\alpha_{\text{GH}} = \frac{[\text{GH}]}{[\text{GH}_2^+] + [\text{GH}] + [\text{G}^-]} \quad (6)$$

$$\alpha_{\text{G}^-} = \frac{[\text{G}^-]}{[\text{GH}_2^+] + [\text{GH}] + [\text{G}^-]} \quad (7)$$

Substitution of Eqs. (2) and (4) into Eq. (5) yields Eq. (8).

$$\alpha_{\text{GH}_2^+} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad (8)$$

Similarly, α_{GH} and α_{G^-} are correlated to Ka and [H⁺] by Eqs. (9) and (10), respectively.

$$\alpha_{\text{GH}} = \frac{\alpha_{\text{GH}_2^+} K_{a1}}{[\text{H}^+]} \quad (9)$$

$$\alpha_{\text{G}^-} = \frac{\alpha_{\text{GH}_2^+} K_{a1} K_{a2}}{[\text{H}^+]^2} \quad (10)$$

Figure 2 shows the fractions of $\alpha_{\text{GH}_2^+}$, α_{GH} and α_{G^-} calculated from Eqs. (8)-(10) as a function of pH. In the pH range from 4 to 8, α_{GH} results in 1. At a pH lower than 4, $\alpha_{\text{GH}_2^+}$ gradually increases with a decrease of pH. In the basic solution, the α_{G^-} value increases with increasing pH. The dissociation of glycine can be strictly controlled by the pH of the solution.

Dispersibility of ceria particles

The dispersibility of the calcined ceria particles in a 2 vol% suspension with and without glycine at pH 2, 4 and 8 was evaluated by measuring the length of phase separation into a clear solution and a concentrated suspension as a function of settling time [19]. Glycine of 0.05-5 mass% against ceria was added to the suspensions. The zeta potentials of colloidal ceria particles with 0.1 mass% glycine were also measured at pH 2, 4 and 8.

Results and Discussion

Zeta potential of ceria powder

Figure 3 shows the zeta potential of the as-calcined ceria powder. The ceria particles were charged positively at 12 mV at pH 2, and charged negatively at -27 mV at pH 8. The isoelectric point was pH 3.0. Addition of glycine to the ceria suspensions increased the zeta potential to positive values. In particular, 0.1 mass% glycine enhanced effectively the zeta potential in the

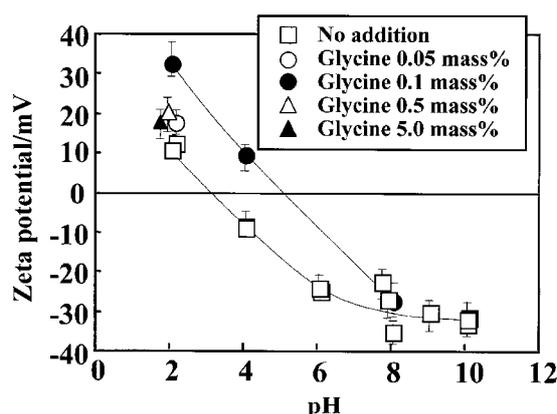


Fig. 3. Zeta potential of ceria powder in the suspensions with and without glycine as a function of pH.

acidic suspensions and shifted the isoelectric point to pH 5.1. The above result indicates the adsorption of glycine onto the surfaces of ceria particles.

Figure 4 shows the possible interactions between the ceria surface and glycine. In the suspension at pH 2.0, Ce-OH_2^+ sites are formed by the reaction of $\text{Ce-OH} + \text{HCl} \rightarrow \text{Ce-OH}_2^+ + \text{Cl}^-$. The ceria surface also reacts with OH^- ions to produce Ce-O^- sites ($\text{CeOH} + \text{OH}^- \rightarrow \text{Ce-O}^- + \text{H}_2\text{O}$). The number of Ce-OH_2^+ sites is greater than that of Ce-O^- sites at a pH below 3, explaining the positively charged surface in the acidic suspension. On the other hand, glycine dissociates into 69% GH_2^+ and 31% GH (Fig. 2). The localization of electrons in GH_2^+ ions produces $\text{O}^{\delta-}$ and $\text{C}^{\delta+}$ atoms. The $\text{O}^{\delta-}$ atoms are attracted to the positively charged Ce-OH_2^+ sites, suggesting an increased positive charge of ceria particles with the addition of glycine. The adsorption of O^- in GH onto Ce-OH_2^+ site produces no increase of positive charge of the ceria surface. However, the interaction between negative Ce-O^- sites and N^+ in GH_2^+ contributes to an increase in the surface charge to a positive value because of the disappearance of negative Ce-O^- sites with the adsorption of GH_2^+ . In the suspension at pH 4, the number of Ce-O^- sites becomes greater than that of Ce-OH_2^+ sites, explaining the negative value of the zeta potential in Fig. 3. The fraction of GH increases to 98% at pH 4.0. However, the adsorption of electrically-neutral GH onto a ceria surface results in no increase of surface charge of ceria particles. The slight increase of the zeta potential of ceria particles with the addition of glycine at pH 4.0 may be due to the interaction of GH_2^+ of 2% and Ce-O^- sites. The number of Ce-O^- sites increases more at pH 8.0. Glycine consists of 98% GH and 2% G^- . No significant change in the zeta potential with the addition of glycine at pH 8.0 is related to the adsorption of electrically-neutral GH and the electrostatical repulsion between negatively-charged ceria surfaces and G^- ions.

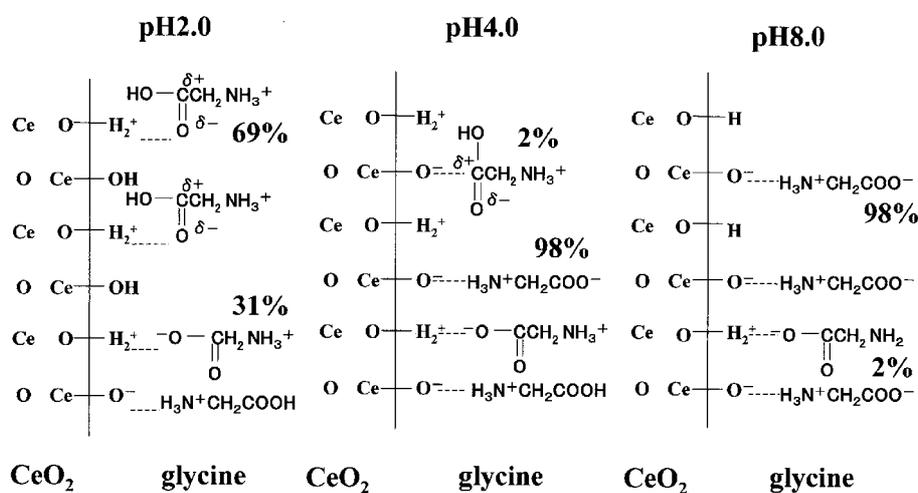


Fig. 4. Schematic illustration of interactions between ceria surface and glycine at pH 2, 4 and 8.

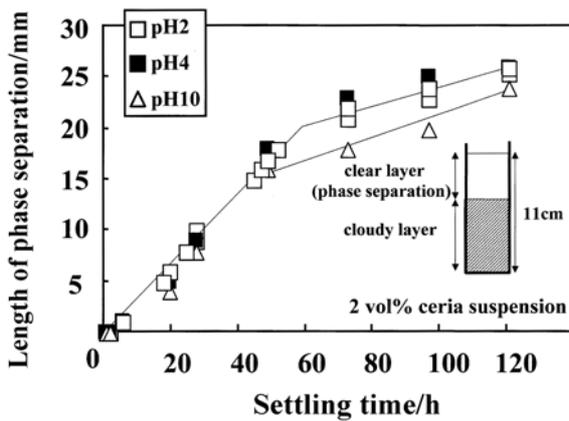


Fig. 5. Length of phase separation in the sedimentation test for ceria suspensions at pH 2, 4 and 10.

Dispersibility of ceria particles

Figure 5 shows the length of phase separation of 2 vol% ceria suspensions as a function of settling time. As seen in Fig. 3, the ceria particles were charged positively at pH 2 and negatively at pH 4 and 10. These results in Fig. 5 indicate little influence of surface charge on the dispersibility of the nanometer-sized ceria particles. The decrease of particle size is accompanied by a decrease of the repulsive energy between charged particles, resulting in a decrease of the primary maximum of the interaction energy (summation of the repulsive energy and van der Waals energy) as a function of distance between two particles [18]. The result in Fig. 5 suggests a difficulty of dispersion of 15 nm-ceria particles by electrostatic repulsive energy.

Figure 6 shows the effect of glycine additions on the dispersibility of ceria particles at pH 2.0. Addition of glycine suppressed the phase separation of ceria suspensions. This result is closely related to the adsorption of glycine (Fig. 4) onto ceria surfaces and the enhancement of zeta potential. The amount of glycine added had no influence on the dispersibility of the ceria particles. A similar suppression effect of glycine on the

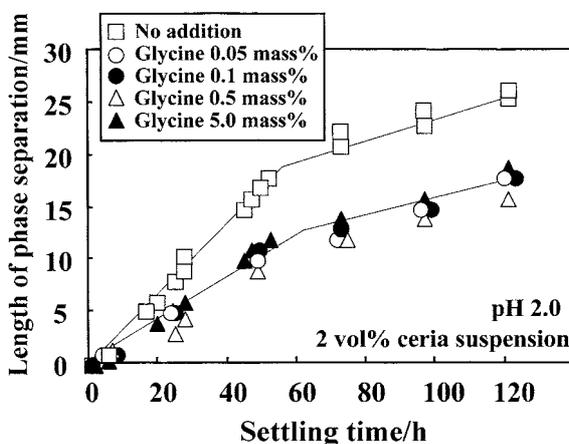


Fig. 6. Influence of glycine addition on the length of phase separation in the sedimentation test for ceria suspensions at pH 2.

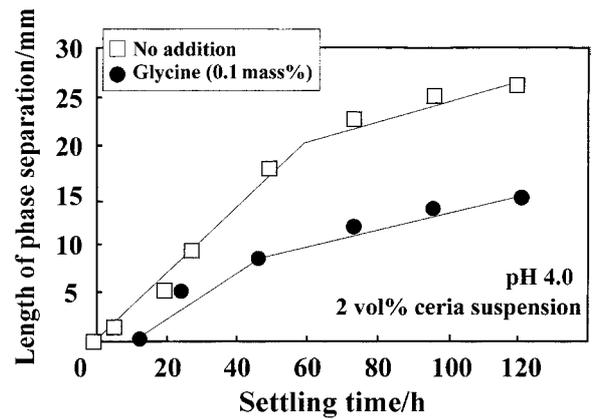


Fig. 7. Length of phase separation in ceria suspensions with and without glycine at pH 4.

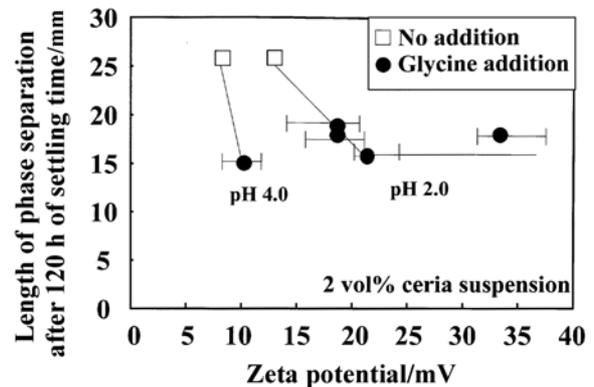


Fig. 8. Relationship between the length of phase separation after 120 h of settling time and zeta potential of ceria particles with and without glycine.

phase separation was measured for the ceria suspension at pH 4.0 (Fig. 7). However, rapid phase separations occurred within 200 minutes for the ceria suspensions with and without glycine at pH 8. Figure 8 shows the relationship between zeta potential of ceria particles and the length of phase separation after 120 h of settling time. The suppression of phase separation with the addition of glycine to the ceria particles with a low zeta potential reflects the importance of the steric effect of the adsorbed glycine.

Conclusions

- (1) The dispersibility of 15 nm-size ceria particles with an isoelectric point at pH 3.0 was not influenced by the surface charge in the suspensions at pH 2-10.
- (2) The addition of glycine of 0.05-5 mass% against ceria particles enhanced the zeta potential of ceria particles to positive values in acidic suspensions.
- (3) The phase separation of ceria suspensions at pH 2.0 and 4.0 was suppressed by the steric stabilization effect of adsorbed glycine. In the basic suspension at pH 8.0, no influence of glycine was measured on the phase separation of the suspension.

References

1. F.F. Lange, *J. Am. Ceram. Soc.* 72[1] (1989) 3-15.
2. I.A. Aksay, *Ceram. Inter.* 17 (1991) 267-274.
3. J.A. Lewis, *J. Am. Ceram. Soc.* 83[10] (2000) 2341-2359.
4. Y. Hirata, S. Matushita, Y. Ishihara, and H. Katsuki, *J. Am. Ceram. Soc.* 74[10] (1991) 2438-2442.
5. V.A. Hackly, *J. Am. Ceram. Soc.* 80[9] (1997) 2315-2325.
6. Y. Hirata, J. Kamikakimoto, A. Nishimoto, and Y. Ishihara, *J. Ceram. Soc. Jpn.* 100[1] (1992) 7-12.
7. Y. Hirata, A. Nishimoto, and Y. Ishihara, *J. Ceram. Soc. Jpn.* 100[8] (1992) 983-990.
8. J. C. Cerasano III, and I. A. Aksay, *J. Am. Ceram. Soc.* 71[4] (1988) 250-255.
9. J-M Cho, and F. Dogan, *J. Mater. Sci.* 36[10] (2001) 2397-2403.
10. S. Baklouti, C. Pagnoux, T. Chartier, and J.F. Baumard, *J. Eur. Ceram. Soc.* 17[12] (1997) 1387-1392.
11. A. Mukherjee, B. Maiti, A.D. Sharma, R.N. Basu, and H.S. Maiti, *Ceram. Inter.* 27[7] (2001) 731-739.
12. H. Shan, and Z. Zhang, *Br. Ceram. Trans.* 95[1] (1996) 35-38.
13. A. Dietrich, and A. Neubrand, *J. Am. Ceram. Soc.* 84[4] (2001) 806-812.
14. Y. Hirata, I. Haraguchi, and Y. Ishihara, *J. Ceram. Soc. Jpn.* 98[9] (1990) 951-956.
15. Y. Hirata, I. Haraguchi, and Y. Ishihara, *J. Mater. Res.* 7[9] (1992) 2572-2578.
16. A. Dietrich, A. Neubrand, and Y. Hirata, *J. Am. Ceram. Soc.* 85[11] (2002) 2719-2724.
17. Y. Hirata, S. Tabata, and J. Ideue, *J. Am. Ceram. Soc.* 86[1] (2003) 5-11.
18. Y. Hirata, S. Nakagama, and Y. Ishihara, *J. Ceram. Soc. Jpn.* 98[4] (1990) 316-321.
19. I.A. Aksay, and R. Kikuchi, *Science of Ceramic Chemical Processing*, edited by L.L. Hench and D.R. Ulrich (John Wiley & Sons, Inc., New York, 1986) pp. 513-521.
20. *Kagaku Binran Kisoohen I*, edited by the Chemical Society of Japan (Maruzen Co., Tokyo, 1993) p. 432.