Colloidal Ceramic Processing of Nano-, Micro-, and Macro-Particulate Systems

Edited by
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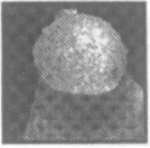
Colloidal Ceramic Processing of Nano-, Micro-, and Macro- Particulate Systems

Proceedings of the Colloidal Ceramic Processing: Nano-, Micro-, and Macro-Particulate Systems held at the 105th Annual Meeting of The American Ceramic Society, April 27–30, 2003 in Nashville, Tennessee

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Proceedings of the Colloidal Ceramic Processing: Nano-, Micro-, and Macro-Particulate Systems held at the 105th Annual Meeting of The American Ceramic Society, April 27–30, 2003 in Nashville, Tennessee

COVER PHOTO: A single silicon nitride spray-dried particle sits on top of a commercial tip for atomic force microscopy evaluation is courtesy of H. Kamiya, S. Matsui and T. Kakui and appears as part of figure 2 in their paper "Analysis of Action Mechanism of Anionic Polymer Dispersant with Different Molecular Structure in Dense Silicon Nitride Suspension by using Colloidal Probe AFM" which begins on page 83.

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Contents

Preface

This volume of Ceramic Transactions consists of papers presented at the International Symposium on Colloidal Ceramic Processing which was held during the 105th Annual Meeting of The American Ceramic Society in Nashville, Tennessee, April 27-30, 2003. The papers summarize the recent developments in colloidal ceramic processing and cover a broad range of subjects including nano-, micro-, and macro-particulate systems. The editors would like to thank the ACerS Basic Science Division for their financial support for this symposium.

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DISPERSIBILITY OF NANOMETER-SIZED CERIA PARTICLES

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ABSTRACT

Nanometer-sized ceria particles (average diameter of 15 nm, calculated from specific surface area) were dispersed at 2 vol% solid in aqueous solutions with glutamic acid and lysine of 0.05-5.0 mass% against ceria at pH 2.0-10.0. The ceria particles without amino acid were charged in the range from 12 to −34 mV at pH 2-10 and no effect of charge on the dispersibility of the powder was seen. A small amount of the amino acid was adsorbed on the positively charged ceria particles at pH 2.0 and increased the zeta potential. Addition of glutamic acid and lysine enhanced the dispersibility of the nanometer-sized ceria particles by electrosteric stabilization.

INTRODUCTION

Colloidal processing comprises of the dispersion of fine ceramic particles in a liquid medium and subsequent consolidation of the colloidal particles [1-4]. This assists in producing a uniform microstructure and high packing density for the powder compact. The dispersibility of the colloidal suspension affects both the sintering behavior and resultant properties of the densified ceramics. Dispersants such as polyacrylic acid [5, 6], 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 high content of ceramic powder and suitable viscosity. When the size of colloidal particles becomes smaller, controlling the properties of the colloidal suspension becomes difficult. This is mainly due to the increased interparticle interaction.i.e., the high viscosity at a low solid content, the low dispersibility of colloidal particles due to increased attractive force and the large amount of dispersant required to

cover the high specific surface area of the colloidal particles [11-16]. A method to solve these problems is by finding a low molecular weight dispersant with good dispersibility. The following criteria were looked into a possible dispersant for the nanometer-sized particles : (1) the size ratio of the established dispersant to the submicrometer-sized particles in a well-dispersed suspension should be kept in a nanometer-sized particle suspension (steric stabilization effect) [7, 8, 17] and (2) the low molecular weight dispersant should be highly charged compared to the nanometer-sized particles to give a strong electrostatic stabilization effect [18, 19]. Thus, amino acid with the two types of ionizable groups (carboxyl and amino groups) can be a good choice as the dispersant. These ionized groups provide the adsorbtion onto particle surfaces and the electrostatic repulsion, depending on the pH of the suspension. Here, a nanometer-sized ceria powder was dispersed in an aqueous solution with glutamic acid and lysine to investigate their interactions.

EXPERIMENTAL PROCEDURE
Ceria powder

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

Drying or calcination temperature (°C)	Specific surface area ($m^{2 \cdot} g^{-1}$)	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
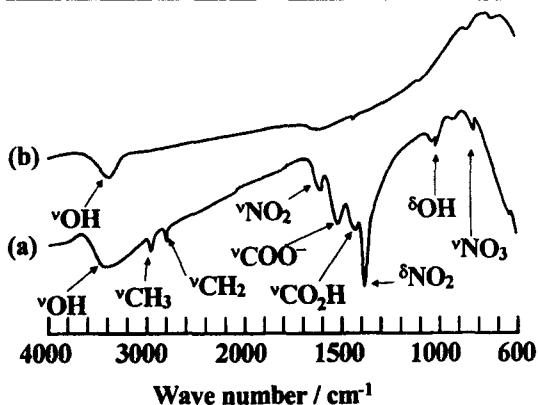
Fig. 1 Infrared spectra of (a) ceria powder and (b) ceria powder calcined at 500°C.

A fine ceria powder was collected by drying a commercial ceria suspension (Nyacol Nano Technologies, Inc., MA, USA) using rotary evaporator. Figure 1 (a) shows the infrared spectrum of the dried ceria powder. HNO_3 and CH_3COOH in the starting suspension remained on the surface of dried ceria powder. Thermo Gravimetric Differential Thermal Analysis (TG-DTA) of the dried ceria powder showed 9.8 % of 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 HNO_3 and CH_3COOH were removed by calcination. Table I indicates the influence of heating temperature on the specific surface

Colloidal Ceramic Processing

area. The specific surface area decreased drastically for the ceria calcined at 700 °C. The diameter (D) of equivalent spherical ceria particle was determined from the specific surface area (S) and powder density (ρ) using the relationship of D=6/ρS. For these experiments, 15 nm ceria powder calcined at 500 °C was used.

Dispersant

In Table II the chemical properties of glutamic acid and lysine used are shown [20]. Glutamic acid and lysine have the molecular length of 1.1– 1.2 nm and provide a size ratio of 0.07– 0.08 to the diameter of ceria particle. The isoelectric point for equal charge of NH_3^+ and COO^- of glutamic acid and lysine was pH 3.22 and 9.47, respectively. The dissociation of glutamic acid (GH_2) is seen in Eqs. (1) (2)

Table II. Chemical properties of glutamic acid and lysine

Property	Glutamic acid	Lysine
Chemical formula	HOOC(CH₂)₂CHCOOH NH₂	H₂N(CH₂)₄CHCOOH NH₂
Purity (mass%)	99	99
Molecular weight	147.13	146.19
Molecular length (nm)	1.1	1.2
Isoelectric point	3.22	9.47
Solubility	water soluble	water soluble
pKa₁	2.19	2.20
pKa₂	4.25	8.90
pKa₃	9.67	10.28

and (3). Ka represents the equilibrium contant.

$$GH_3^+ \underset{}{\overset{Ka_1}{\rightleftharpoons}} GH_2 + H^+ \tag{1}$$

$$GH_2 \underset{}{\overset{Ka_2}{\rightleftharpoons}} GH^- + H^+ \tag{2}$$

$$GH^- \underset{}{\overset{Ka_3}{\rightleftharpoons}} G^{2-} + H^+ \tag{3}$$

From Eqs. (1)-(3), the dissociated fraction (α) of GH_3^+ to the total concentration of neutral and ionized glutamic acid is related to Ka and $[H^+]$ by Eq. (4).

$$\alpha_{GH_3^+} = \frac{[GH_3^+]}{[GH_3^+] + [GH_2] + [GH^-] + [G^{2-}]} = \frac{[H^+]^2}{[H^+]^2 + Ka_1[H^+] + Ka_1Ka_2} \tag{4}$$

Similarly, α_{GH_2}, α_{GH^-} and $\alpha_{G^{2-}}$ are given by Eqs. (5), (6) and (7), respectively.

$$\alpha_{GH_2} = \frac{\alpha_{GH_3}{}^+ Ka_1}{[H^+]} \tag{5}$$

$$\alpha_{GH}{}^- = \frac{\alpha_{GH_2}{}^+ Ka_1 Ka_2}{[H^+]^2} \tag{6}$$

$$\alpha_{G}{}^{2-} = \frac{\alpha_{GH_2}{}^+ Ka_1 Ka_2 Ka_3}{[H^+]^3} \tag{7}$$

Figure 2 shows the fractions of $\alpha_{GH_3}{}^+$, α_{GH_2}, $\alpha_{GH}{}^-$, and $\alpha_{G}{}^{2-}$ calculated by Eqs. (4)-(7) as a function of pH. With an increase of pH, the dominant species changes as follows: $GH_3^+ \rightarrow GH_2 \rightarrow GH^- \rightarrow G^{2-}$. Similarly, the dissociation of lysine (LH) is expressed by Eqs. (8)- (10).
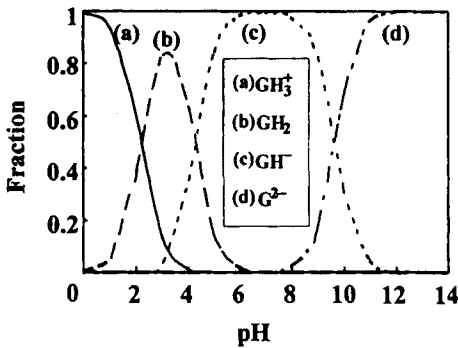
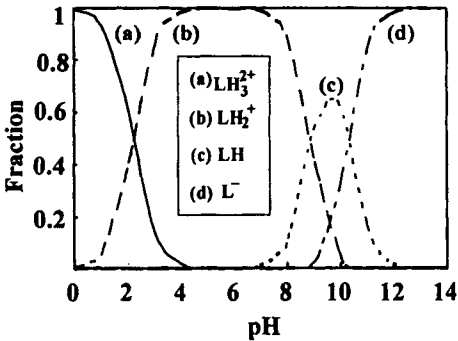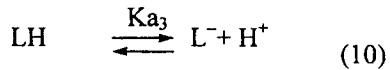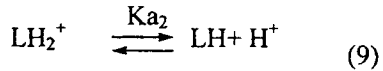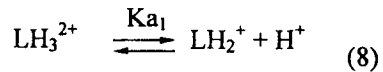Fig. 2 Fraction of dissociated glutamic acid (GH$_2$) as a function of pH.

Fig. 3 Fraction of dissociated lysine (LH) as a function of pH.

$$LH_3^{2+} \xrightarrow{\ Ka_1\ } LH_2^+ + H^+ \tag{8}$$

$$LH_2^+ \xrightarrow{\ Ka_2\ } LH + H^+ \tag{9}$$

$$LH \xrightarrow{\ Ka_3\ } L^- + H^+ \tag{10}$$

The equilibrium constants are shown in Table II. The dissociated fractions (α) of LH_3^{2+}, LH_2^+, LH and L^- are shown in Figure 3. The dominant species changes as follow with increasing pH: $LH_3^{2+} \rightarrow LH_2^+ \rightarrow LH \rightarrow L^-$. In the pH range from 8 to 12, LH_2^+, LH and L^- coexist in a solution.

Dispersibility of ceria particles

Dispersibility of the calcined ceria particles in 2 vol% suspension with and without amino acid at pH 2-10 were evaluated by measuring the length of the phase separation into a clear solution and a concentrated suspension as a function of settling time [19]. Glutamic acid and lysine (0.05-5 mass% ceria) was added to the suspensions. The zeta

potential of colloidal ceria particles with and without the amino acid was measured at pH 2-10 at a constant ionic strength of 0.01 M NH$_4$NO$_3$ (Rank Mark II, Rank Brothers Ltd., Cambrige,UK).

RESULTS AND DISCUSSION
Zeta potential of ceria powder

Figure 4 shows the zeta potential of the calcined ceria powder. The ceria particles were charged positively with 12 mV at pH 2, and charged negatively with -30 mV at pH 8. The isoelectric point was pH 3.0. Addition of 0.1 mass% glutamic acid to the ceria increased the ze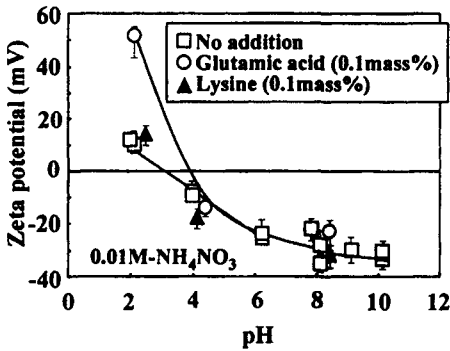ta potential to 52 mV at pH 2.0. However, no significant influence of glutamic acid addition on the zeta potential of ceria was measured at pH 4.0 and 8.0. Figure 4 also shows the influence of lysine (0.1 mass%) on the zeta potential of ceria suspension. Figure 5 shows the relationship between the amount of glutamic acid and lysine added and the zeta potential of ceria particles at pH 2.0. The zeta potential of ceria particles showed a maximum at 0.1 mass% glutamic acid and 0.5 mass% lysine. This result indicates a strong interaction between ceria surfaces and the amino acid added.

Fig. 4　Zeta potential of ceria powder in the suspensions with and without glutamic acid and lysine as a function of pH.

Figure 6 shows the possible interactions between ceria surface and amino acid. In the suspension at pH 2.0, Ce-OH$_2^+$ sites are formed by the reaction, Ce-OH + HCl → Ce-OH$_2^+$ + Cl$^-$. The ceria surface also reacts with OH$^-$ ions to produce Ce-O$^-$ sites (CeOH + OH$^-$→Ce-O$^-$ + H$_2$O). The number of Ce-OH$_2^+$ sites is greater than that of Ce-O$^-$ sites at pH below 3, explaining the positively charged surface at pH 2. On the other hand, glutamic acid dissociates into 61 % GH$_3^+$ and 39 % GH$_2$ (Figure 2).
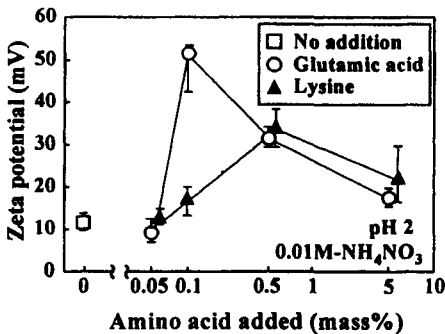
Fig. 5　Zeta potential of ceria particles in the suspensions at pH 2.0 as a function of the amount of added glutamic acid and lysine.

The localization of electrons in carboxyl group of GH_3^+ ion produces $O^{\delta-}$ and $C^{\delta+}$ atoms. The $O^{\delta-}$ atoms are attracted to the positively charged $Ce-OH_2^+$ site, suggesting the increased positive charge of ceria particles. The adsorption of O^- in GH_2 onto $Ce-OH_2^+$ site produces no increase of positive charge of ceria surface. However, the interaction between negative $Ce-O^-$ site and N^+ in GH_3^+ contributes to increase the surface charge to positive value because of the disappearance of negative $Ce-O^-$ sites with adsorption of GH_3^+. In the suspensions at pH 4 and 8, the number of $Ce-O^-$ sites becomes greater than that of $Ce-OH_2^+$ sites, explaining
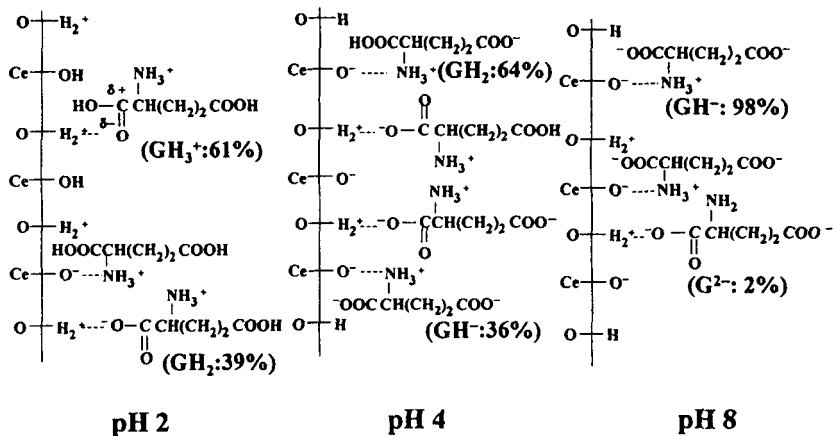
Fig. 6   Schematic illustration of possible interactions between ceria surface and glutamic acid at pH 2, 4 and 8.
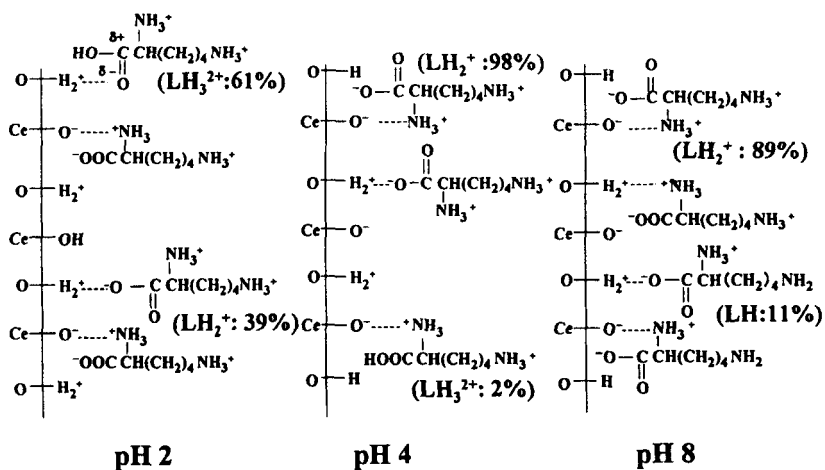
Fig. 7   Schematic illustration of possible interactions between ceria surface and lysine at pH 2, 4 and 8.