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Interaction of Amino Acids and Silica-Containing Mixed-Oxide Surfaces in Aqueous Solutions

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The addition of alumina, magnesia, or titania to silica has been effective on the adsorption of amino acids. The initial pH of amino acid solution and the pore-size distribution of the mixed oxide had an influence on the adsorption; the adsorption mechanism has been discussed.

As a biotechnological production has been developed, the effective separation and purification of objective bioproducts will be required. A chromatographic technique based on the interaction between an objective material and the solid surface of adsorbent may well become the most feasible technique for this purpose among various advanced methods. However, the study on the adsorption of amino acid on metal oxide has not been attempted so much except titania1) and iron(III) hydrooxide.2) We have been interested in the preparation of silica-containing mixed-oxide gels through wet processes, and their characterization and applications to catalyst3) and adsorbent,4-6) making use of their large surface areas kept up to temperatures above 800 °C.7) Some of these gels exhibited also good adsorption ability for nitrogen-containing dyes and amines in aqueous solutions.8,9) In connection with the technique described above we have investigated the adsorption behavior of typical amino acids in aqueous solutions on silica-alumina (SA), silica-magnesia (SM), and silica-titania (ST) gels.

Silica-containing mixed-oxide gel was precipitated from the mixture of sodium metasilicate solution acidified with hydrochloric acid to pH 1 in advance and aluminum, magnesium, or titanium chloride solution by adding sodium hydroxide up to the prescribed pH at room temperature. After aging for 10 h, the resultant precipitate was filtered by suction, thoroughly washed with deionized water, and then dried in an oven at 110 °C overnight. The dried gel was sieved to 20-42 mesh size (average diameter ca. 0.5 mm) after grinding. The crystalline state and thermal behavior of mixed-oxide gel were investigated by means of an X-ray diffraction (XRD) technique, and differential thermal analysis and thermogravimetry simultaneously performed, respectively. The surface area measurement of gel was carried out by applying the BET equation to adsorption isotherm of nitrogen at -196 °C. The pore-size distribution curve of gel was obtained by applying the Cranston-Inkley equation to this adsorption isotherm.10) The point of zero charge (pzc) of gel was

Table 1. Adsorption percentage of silica-containing mixed-oxide gels of the optimum composition for the amino acid

Gel	Composition / mol%	Specific surface area / $m^2 g^{-1}$	Amino acid adsorbed	Adsorption / %
SA	silica 25 alumina 75	32	L-GLU	71
SM	silica 50 magnesia 50	492	GLY	27
ST	silica 75 titania 25	222	L-LYS	78[a]

a) Amount of adsorbent: 50 mg.

determined from the surface charge density calculated by means of a potentiometric titration.[11] Laboratory tests on three amino acids, L-glutamic acid (acidic amino acid, L-GLU), glycine (neutral amino acid, GLY), L-lysine (basic amino acid, L-LYS) were conducted by shaking 200 mg of adsorbent with 50 cm^3 of 50 mg dm^{-3} of amino acid solution at 25 °C for 24 h. After agitation, the solution was filtered through a 1.0 μm membrane filter. The concentration of amino aicd was then determined by using a total organic carbon analyzer and the adsorption percentage was calculated from the difference between two concentrations before and after the test.

The adsorption abilities of silica-containing binary gels for amino acid in aqueous solution are summarized in Table 1. The following combinations were best among those examined; SA of mole ratio 1:3 for L-glutamic acid, SM of mole ratio 1:1 for glycine, and ST of mole ratio 3:1 for L-lysine. The adsorption ability of SA arised from the high ability of pure alumina because pure silica hardly showed the ability. The abilities of these three gels for glycine were all low, compared with those for the other amino acids in the present work, despite the effect of mixing magnesia with silica on the adsorption ability was recognized to some extent. Both silica and titania gels showed somewhat the ability for L-lysine which was greatly improved by mixing of the two in the wide extent of composition. Okazaki et al. also reported the high ability of titania for basic amino acids due to the surface OH groups showing weak Brönsted acidity.[1] Silica-titania gel showed solid acidity and cation-exchange ability.[6,12] As in the adsorption of amine,[9] silica-titania adsorbed L-lysine mainly by the mechanism of ion-exchange between amino group in aqueous solution and sodium ion on the surface of gel originated from the starting material (sodium metasilicate) and the precipitant (sodium hydroxide).

Figure 1 shows the change of XRD patterns of SA, SM, and ST gels by the heat treatment. SA gel was mainly composed of amorphous aluminum hydroxide, which was kept as it was up to 900 °C. The weight loss of the gel due to dehydration proceeded largely up to 600 °C but afterwards slowly up to 1000 °C. The specific surface area of the gel was smaller than those of the other gels (Table 1), because the aluminum hydroxide particles covered and stuffed the micropores of silica. There were two broadened profiles in the XRD pattern of as-prepared SM: one was due to silica gel and another magnesium hydroxide. The dehydration of this binary gel was almost completed by 300 °C and the exothermic peak in the DTA curve was found at 870 °C attributed to the formation of magnesium hydroxide ($MgSiO_3$). The deposit of magnesium hydroxide particles onto the micropores of silica caused the surface area of silica to increase further by the occurrence of uneveness of the inner surface of micropores. We could observe only the broadened profile of silica gel in the XRD pattern of ST gel. The weight loss of the gel due to dehydration was remarkable by 300 °C. The thermal product of the gel at 900 °C was the mixture of α-tridymite and rutile. The micropores of silica gel here were not so much developed by the precipitation of titania particles. The specific surface area of ST gel was lower than that of SM gel, as shown in Table 1.

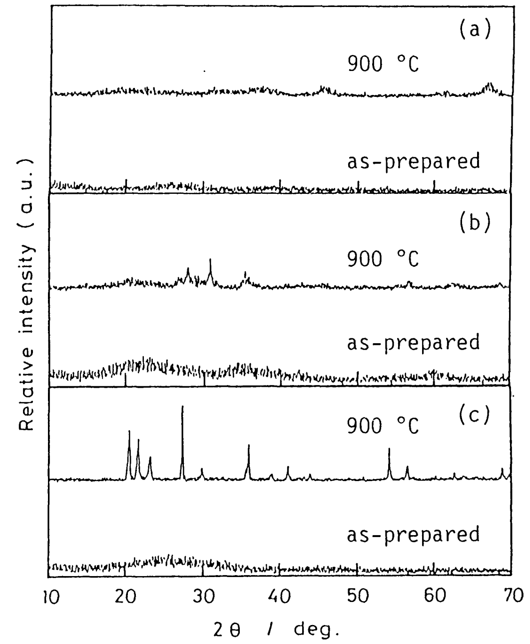

Fig. 1. X-Ray diffraction patterns of the binary oxide gels.
(a): SA2575, (b): SM5050, (c): ST7525

Figure 2 shows that the adsorption of amino acids on the binary gels was significantly affected by the pH of aqueous solution. L-glutamic acid was most adsorbed on SA gel at around pH 2 being lower than the pzc (pH 4.61) of the gel, where the gel surface was positively charged. This adsorption proceeded by the mechanism of the electrostatic bond between negative carboxyl ion of amino acid and positively charged gel-surface, while, the adsorption did not occur in the solution of pH above the pzc where the surface charge of gel became negative. Aoki et al. explained similarly that the adsorption of acidic amino acid onto iron (III) hydroxide occurred by the electrostatic bond.2) The adsorption of electrically neutral glycine on SM gel occurred likely by the physical adsorption via hydrogen bond and/or van der Waals bond which was not affected by the pH of solution. However, the decrease in the adsorption percentage of glycine above pH 10 was caused by the dissolution of silica component of this binary gel into basic solution.13) Moreover, it was noteworthy that the reduction of adsorption ability of ST gel for L-lysine was recognized in the range of both sides of pH 8.2 above the pzc (pH 6.72), that is, the adsorption percentage here was maximum at around pH 8.2. At higher range than pH 6.72 this adsorption should be advanced by the mechanism of cation-exchange between basic (cationic) amino acid in solution and sodium ion located on the gel. Okazaki et al. suggested the cation-exchange reaction between basic amino acid and weak Brönsted site at surface OH group on titania.1) The increase in pH of solution might make this ion-exchange reaction easy,12) however, the dissolution of silica component of ST gel into basic solution above pH 10 as well as SM gel caused the adsorption ability to drop on account of diminished porous surface structure of gel suitable for the ad-

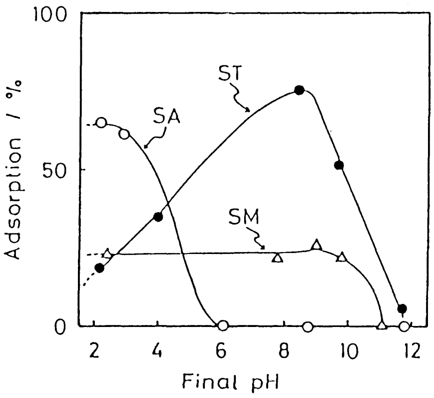

Fig. 2. Effect of pH on the adsorption.
○: L-GLU, △: GLY, ●: L-LYS

Table 2. Change of pore volume of silica-containing mixed-oxide gel by the adsorption of amino acid

Gel	Amino acid adsorbed	Pore diameter / Å	Pore volume / cm^3g^{-1} before adsorption	Pore volume / cm^3g^{-1} after adsorption
SA2575	L-GLU	20-40	0.010	0.020
		40-105	0.028	0.022
SM5050	GLY	20-40	0.162	0.171
		40-105	0.065	0.075
ST7525	L-LYS	20-40	0.090	0.196
		40-105	0.042	0.041

sorption. On the other hand, the reduction of adsorption ability at lower range than pH 6.72 was due to the repulsion between amino group and positively charged gel-structure.

The pore volume of diameter 20-40 Å of SA gel after the adsorption of L-glutamic acid increased but reversely that of diameter 40-105 Å decreased (Table 2). The increase in the pore volume of smaller diameter was probably due to the multi-layers adsorption of amino acid and the deposition of colloidal alumina particles, which was formed by the dissolution of alumina component of SA gel to the acidic amino acid solution (pH 4.2), at the inner surface of mesopores of diameter 40-105 Å. The pore volume of SM gel was not so greatly changed by the adsorption of glycine because of small adsorption amount. Furthermore, the pore volume of ST gel was affected by the adsorption of L-lysine; the increase in the pore volume of diameter 40-105 Å was observed just as in the adsorption of L-glutamic acid on SA gel. This seems to be due to the shrinkage and uneveness of mesopores above 105 Å by the dissolution of silica component of ST gel into the basic amino acid solution (pH 9.1).5)

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