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Zeta Potentials of Metal Oxide Surfaces Modified with Silane Coupling Agents

Kunio Esumi* and Kenjiro Meguro

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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Synopsis. The zeta potentials of metal oxide surfaces modified with silane coupling agents were measured as a function of pH in the suspensions. The methylations of the samples by methyltrimethoxysilane showed lower zeta potential values than those of the samples untreated. On the other hand, the treatment of the samples by two different amino silanes rendered the surfaces more cationic. The stability of the deposited silane layers was low; such a layer was easily removed from alumina and anatase-type titanium dioxide.

Coupling agents for modifying many oxide surfaces have been used to improve the bonding between reinforcements and polymer matrix. To elucidate the modified metal oxide surfaces, Fourier transform infrared spectroscopy and Auger electron spectroscopy have been employed. Chiang and Koenig[1] used Fourier transform infrared spectroscopy to study the orientation of silane coupling agents on glass surfaces. However, when surface treatments are applied to a dispersion system containing porous material in solution, the above techniques become inapplicable. In this case, electrokinetic measurements such as zeta potential could be a useful method to detect changes in surface properties. Indeed, Koh[2] reported the change in surface charge density of alumina coated with (3-aminopropyl)triethoxysilane from streaming potential measurements. However, no systematic study has been made on the electrokinetic effects of metal oxides modified with silane coupling agents.

In this work surface properties of several metal oxides modified with silane coupling agents were investigated by measuring the zeta potentials as a function of pH in aqueous solution.

Three silane coupling agents, (3-aminopropyl)tri-

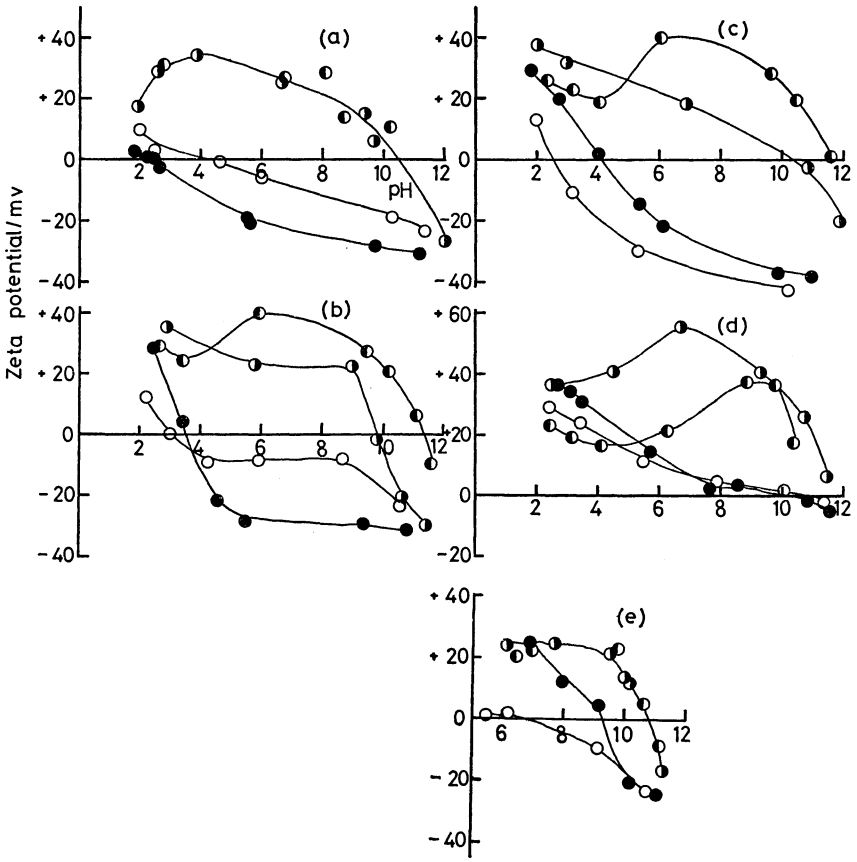

Fig. 1. Zeta potentials of untreated and silane coupling agents treated metal oxides as a function of pH in suspensions: (a) silica, (b) iron oxide, (c) rutile-type titanium dioxide, (d) anatase-type titanium dioxide, (e) alumina; (●) untreated, (○) methyltrimethoxysilane, (◑) (3-aminopropyl)triethoxysilane, (◐) [3-(2-aminoethylamino)propyl]trimethoxysilane.

ethoxysilane, [3-(2-aminoethylamino) propyl] trimethoxysilane, and methyltrimethoxysilane were kindly supplied by Tisso Chemicals, and were used without further purification. Metal oxides employed were titanium dioxide(anatase-type, rutile-type), alumina, iron oxide, and silica supplied by Teikoku Chemicals, Kokusan Chemicals, Titan Chemicals, and Nippon Aerosil Co., respectively.

Coating of silane coupling agents on metal oxide surfaces was carried out with about 3 wt% solution of silane coupling agents in methanol–water mixture (4:1 by volume). Two drops of glacial acetic acid were added to catalyze the hydrolysis. The metal oxide was added and stirred into the silane coupling agent solution for 20 min at room temperature. Then the metal oxide coated with the silane coupling agent was collected and dried in an oven at 80 °C for 10 min.

Measurements of zeta potential for the metal oxides before and after their silane coupling treatments were made using a Pen Kem Laser 500 Zeta Potential. The pH of the suspension containing the metal oxide treated with a silane coupling agent was adjusted with HCl or NaOH.

The stability of untreated and silane coupling agent treated metal oxide suspensions was compared visually in small beakers. The untreated metal oxides were readily dispersible by gentle shaking, whereas the treated metal oxides were initially aggregated. However, they dispersed when the suspensions were treated in an ultrasonic cleaning bath.

Figure 1 depicts zeta potentials of untreated and silane coupling agents treated metal oxides as a function of pH in the suspensions. As can be seen from Fig. 1, the magnitude of zeta potentials for most of the samples treated with methyltrimethoxysilane was smaller over the entire pH range(pH 2—12) than that of untreated samples. This suggests that methylation for the metal oxides affects the electrical double layers to some extent. Further, it was found that the zero point of charge(zpc) for all the samples was not changed significantly after the methyltrimethoxysilane treatment. On the other hand, the zeta potentials of all the samples treated with (3-aminopropyl)-triethoxysilane and [3-(2-aminoethylamino)propyl]trimethoxysilane were positively over a wide pH range. In the case of silica and alumina, no differences of the zeta potentials treated with two kinds of amino silane coupling agents were observed. It is noteworthy

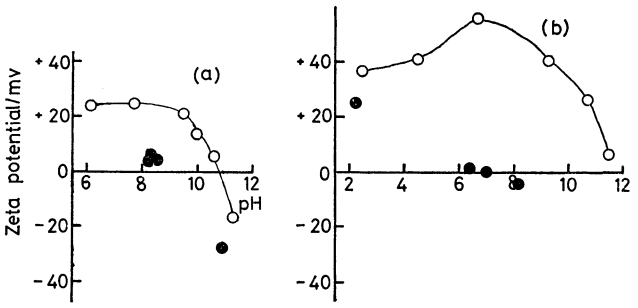

Fig. 2. Change in zeta potential of metal oxide treated with (3-aminopropyl)triethoxysilane: (a) alumina, (b) anatase-type titanium dioxide; (○) immediately, (●) after 1 d.

that the zpc of all the samples treated with two kinds of amino silane coupling agents is shifted to pH 10—12, in spite of the different acid-base character for the metal oxides. These results support the assertion that the polyaminosiloxanes films formed from the hydrolysis of the amino silane coupling agents are coated completely on the metal oxides.

It is also important to study the stability of deposited silane layers on the metal oxides. For this purpose, the samples treated with two kinds of amino silane coupling agents were allowed to stand for one day in aqueous solution a some pH value and then the zeta potential was measured. The results are shown in Fig. 2. The zeta potential after one day became near the original value due to detachment of the silane layers from the metal oxide surface. Especially, as shown in Fig. 2, the changes in the zeta potential after one day were remarkably significant for alumina and anatase-type titanium dioxide coated with the amino silane. Chiang and Koenig[1] studied the hydrothermal stability of silica treated with diamino silane coupling agent; they found that the coupling agent was rapidly removed from the silica surface after it was immersed in boiling water.

Accordingly, zeta potential measurement is a useful method to analyze surface properties of metal oxides treated with silane coupling agents.

References

1) C. H. Chiang and J. L. Koenig, *J. Colloid Interface Sci.*, **83**, 361 (1981).
2) W. H. Koh, *J. Colloid Interface Sci.*, **71**, 613 (1979).