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Chemisorbed Species of Alkyl Benzoates on Alumina Surface Studied by Inelastic Electron Tunneling Spectroscopy

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Vibrational spectra of alkyl benzoates dissociatively adsorbed on the alumina surfaces have been measured by inelastic electron tunneling spectroscopy. The analyses of the spectra indicate that ethyl and tert-butyl benzoates are adsorbed as ethoxide or benzoate ions, respectively, by the acid-catalyzed reaction on alumina surfaces.

The vibrational spectroscopy is a useful method for getting information about the adsorbed species onto solid or film surfaces. Inelastic electron tunneling spectroscopy(IETS) is a non-optical vibrational spectroscopy of high sensitivity and excellent resolution and is applicable to the study of surface adsorbates on oxide films.1) The technique of IETS is also demonstratively a powerful tool in the study of surface and interface phenomena by using the metal-oxide-metal (Al-Al_2O_3-Pb) tunnel junctions.

To date the adsorbed species on the alumina surface have been studied for various compounds by this method. In regard to the esters, several compounds, viz. methyl and phenyl sulfonates,2) dialkyl phosphites,3,4) and alkyl carboxylates,5) have been studied and are found to be adsorbed dissociatively on the alumina surfaces. The acids of decomposed products for these esters have been observed as adsorbed species on the alumina surfaces. It is well known that esters are decomposed to the corresponding acids and alcohols by acid or base-catalyzed reactions and that the carboxylic acid esters are decomposed through two processes: one is the fission of acyl-oxygen bond and the other is the fission of alkyl-oxygen bond of the ester molecules.6) Bayman et al.5) have shown that adsorbed species are the only acids produced from the decomposition of carboxylic acid esters on alumina surfaces. On the other hand, the alcohols produced by decomposed esters would also be expected to be adsorbed on the alumina surfaces, just as ethanol is adsorbed as an ethoxide ion onto alumina.7) Therefore, it is important and interesting to study the chemisorption of carboxylic acid esters on alumina surfaces in order to understand the mechanism of ester decomposition. In this letter, we report the adsorbed species by the decomposition of ethyl and tert-butyl benzoates on alumina and the probable decomposition process of those esters on the oxide surface.

The method of junction preparation and the apparatus for measuring the tunneling spectrum have been described in detail previously.[9,10] Aluminium (Mitsuwa Chemicals, 99.999%) was evaporated from a molybdenum boat on a clean glass slide to form three strips(1 mm wide) at a pressure of 10^{-5} Torr(1 Torr = 133.32 Pa). The surfaces of the strips were oxidized in an

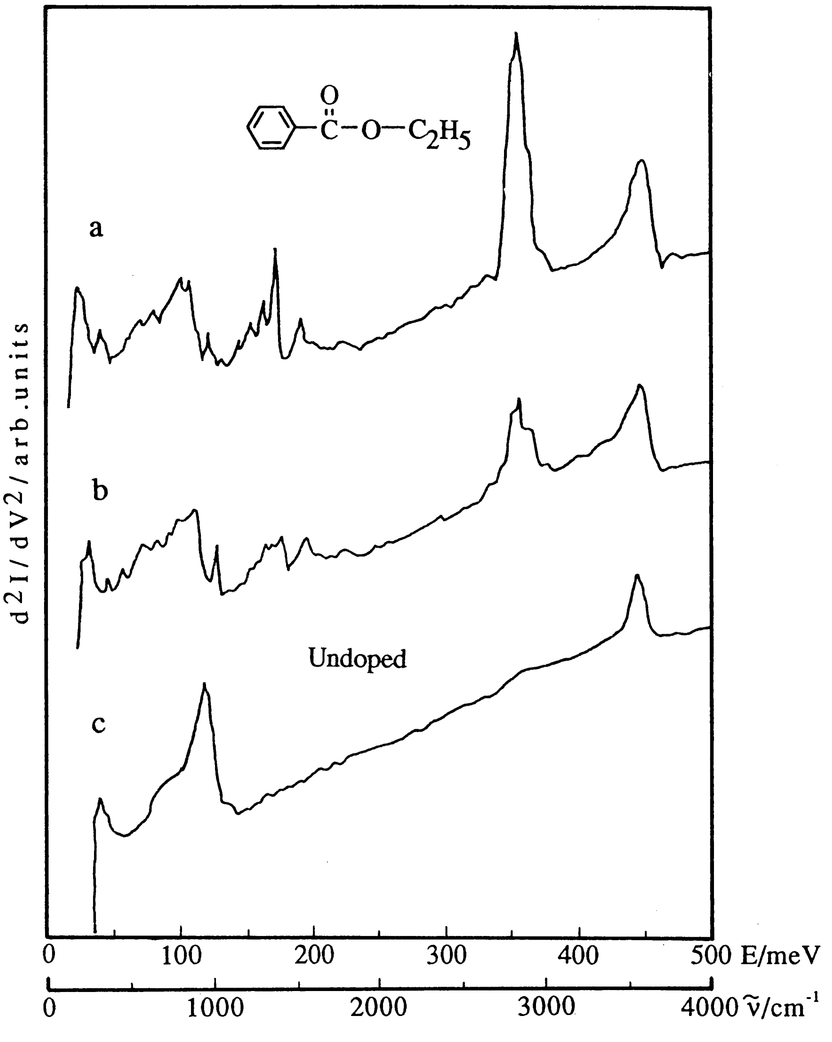

Fig. 1. Inelastic electron tunneling spectra of adsorbed species for ethyl benzoate onto the alumina surface from benzene solution (100.0 mg/ml): doped (a) 1 min and (b) ca.3 s. The spectrum of the undoped junction (c) is also shown for comparison.

oxygen dc glow discharge (400-800 V, 0.075 Torr, 5 mA, 30-45 s) in a bell jar. The slide was removed from the vacuum system and ethyl and tert-butyl benzoates (Tokyo Kasei Organic Chemicals) were allowed to adsorb on the alumina surface of the slide from the benzene solution(100.0 or 10.0 mg/ml) by using the spin doping method at the temperature 24 ± 1 °C. The slide then was returned to the vacuum system and the junction was completed with an evaporated Pb (Wako Chemicals 99.999%) cross strip (1 mm wide). The tunneling spectra were measured at liquid-helium temperature (4.2 K).

The tunneling spectra of adsorbed species for ethyl benzoate onto the Al_2O_3 thin film are shown in Fig. 1. The band shapes and positions of Fig. 1 (a) or (b) differ from those (Fig. 2 (b)) of benzoic acid. The spectra (a) and (b), which are doped for 1 min and ca. 3 s, have the strong bands of the stretching mode of νsCH_3(2890 cm^{-1}) and $\nu asCH_3$(2945 cm^{-1}), and shoulder band of νCH_2(2855 cm^{-1}), respectively. The spectra show also the bands of the deformation mode based on νsCH_3(1439 cm^{-1}) and $\nu asCH_3$ (1771 cm^{-1}), and Al-ethoxide stretching mode at 728 cm^{-1}. These band intensities

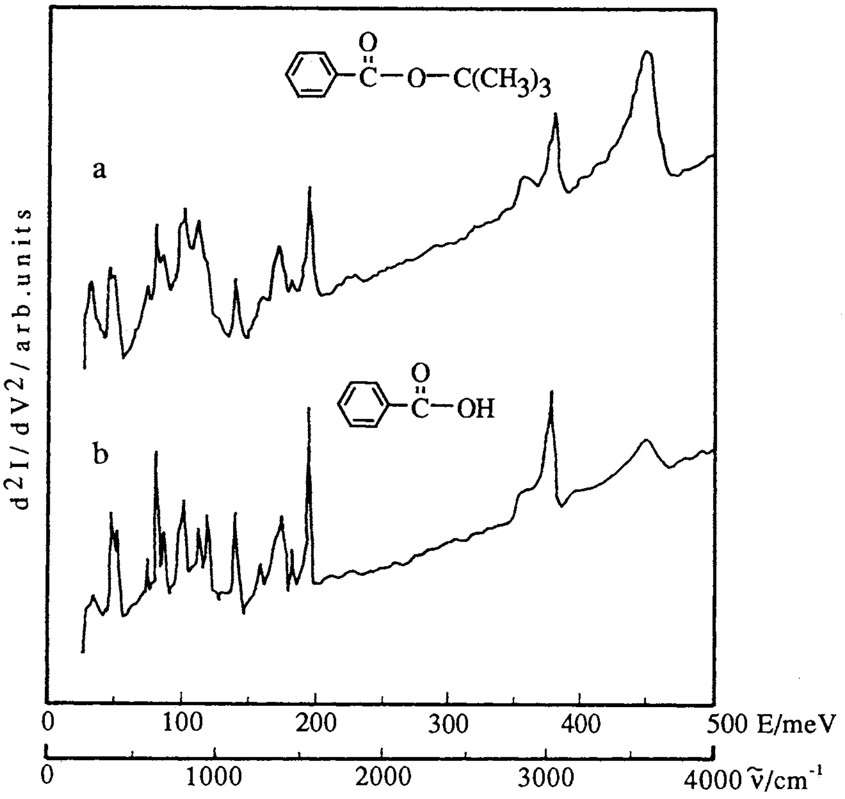

Fig. 2. Tunneling spectra of tert-butyl benzoate absorbed onto alumina film surface from benzene solution (10.0 mg/ml) and of benzoic acid from benzene solution (0.5 mg/ml).

are increased, when the ethyl benzoate is in contact with the alumina surfaces for a long periods of time. The spectrum of adsorbed species for ethyl benzoate is similar to that of adsorbed ethanol from the vapor on the alumina surfaces in band positions and intensities.7,8) Therefore, it can be considered probable that ethyl benzoate in benzene solution (water content is ca. 0.004%) was subjected to acid-catalyzed hydrolysis on alumina surfaces and the ethanol produced by the cleavage of acyl-oxygen bond of the ester was adsorbed as an ethoxide ion on the oxide surfaces. The relative intensity of the ν(OH) band indicates that the background hydroxyl signal is enhanced following formation of the ethoxide ion on alumina surfaces.7,8)

The tunneling spectrum of adsorbed species for tert-butyl benzoate onto the Al_2O_3 surface is shown in Fig. 2. The bands of $\nu sCOO^-$ (1426 cm^{-1}) and $\nu asCOO^-$(1565 cm^{-1}), and the characteristic modes of phenyl group, viz. aromatic CH stretch at 2996-3077 cm^{-1} and strong ring mode at 1601 cm^{-1}, are shown in spectrum Fig.2 (a). And also the spectrum (a) is very similar to that of (b) which shows the adsorbed species of benzoic acid in both band positions and relative intensities. A marked difference was observed in the relative intensity of the ν(OH) mode. Thus, it can be concluded that the tert-butyl benzoate is subjected to hydrolysis by the cleavage of alkyl-oxygen bond on the Al_2O_3 surface and the resulting benzoic acid is adsorbed as benzoate ion on the oxide surface. The cleavage of alkyl-oxygen bond for tert-butyl benzoate is considered having been caused by a bigger number of electrons repelling of the tert-butyl group than those of the ethyl group.

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