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Surface Reaction of Methyl Sulfonates on Alumina Studied by Inelastic Electron Tunneling Spectroscopy

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Vibrational spectra of methyl sulfonates adsorbed onto an alumina surface have been measured by inelastic electron tunneling spectroscopy. The spectra indicate that the sulfonates react with OH groups of the alumina surface and are adsorbed dissociatively onto the alumina surface as sulfonate ions.

Recently there has been an increased interest in a new technique for investigation of the adsorbed species on the oxide surface of a metal-oxide-sample-metal tunneling junction at cryogenic temperatures. The junction which has the sandwich constitution of Al-Al_2O_3-sample-Pb is fabricated by vacuum evaporation and oxidation techniques. The useful range of tunneling spectra extends from 400 to 4000 cm^{-1} and includes all molecular vibrations. Inelastic electron tunneling spectroscopy(IETS) exceeds in sensitivity and resolution, and can detect a small amount of adsorbed molecules as compared with other spectroscopic methods for surface analysis. The tunneling spectra of sulfonic acids showed that these molecules were adsorbed on Al_2O_3 as sulfonate ions.1) The sulfonate ions were adsorbed perpendicularly to the surface as in the case of adsorbed monocarboxylate2) and phosphonate ions 3,4) for those acids. On the other hand, carboxylic esters were decomposed on alumina surfaces to form adsorbed carboxylate ions,5) and also dialkyl phosphites were decomposed on the surface to give adsorbed o-alkyl phosphonate mono- and di-anions.6) The sulfonic esters would also be expected to be decomposed on Al_2O_3 surfaces. Thus, it is important and interesting to study these compounds on alumina surfaces. In this letter, we report the reactions of methyl methanesulfonate and benzenesulfonate on Al_2O_3 surface and the orientation of their species on the oxide surfaces.

The method of junction preparation and the apparatus for measuring the tunneling spectrum have been described in previous papers.7,8) Aluminium (Mituwa 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. The surfaces of the strips were oxidized by an oxygen-dc glow discharge(400-800 V, 75 mTorr, 5 mA, 30 s) in a bell jar. The slide was removed from the vacuum system and methyl methanesulfonate(Kanto Chemicals) or methyl benzenesulfonate (Tokyo Kasei) was adsorbed on the alumina surface from the solution of benzene(1.0-3.0 mg/ml) by using the spin doping method in the temperature range(15-25 °C). The slide was then returned to

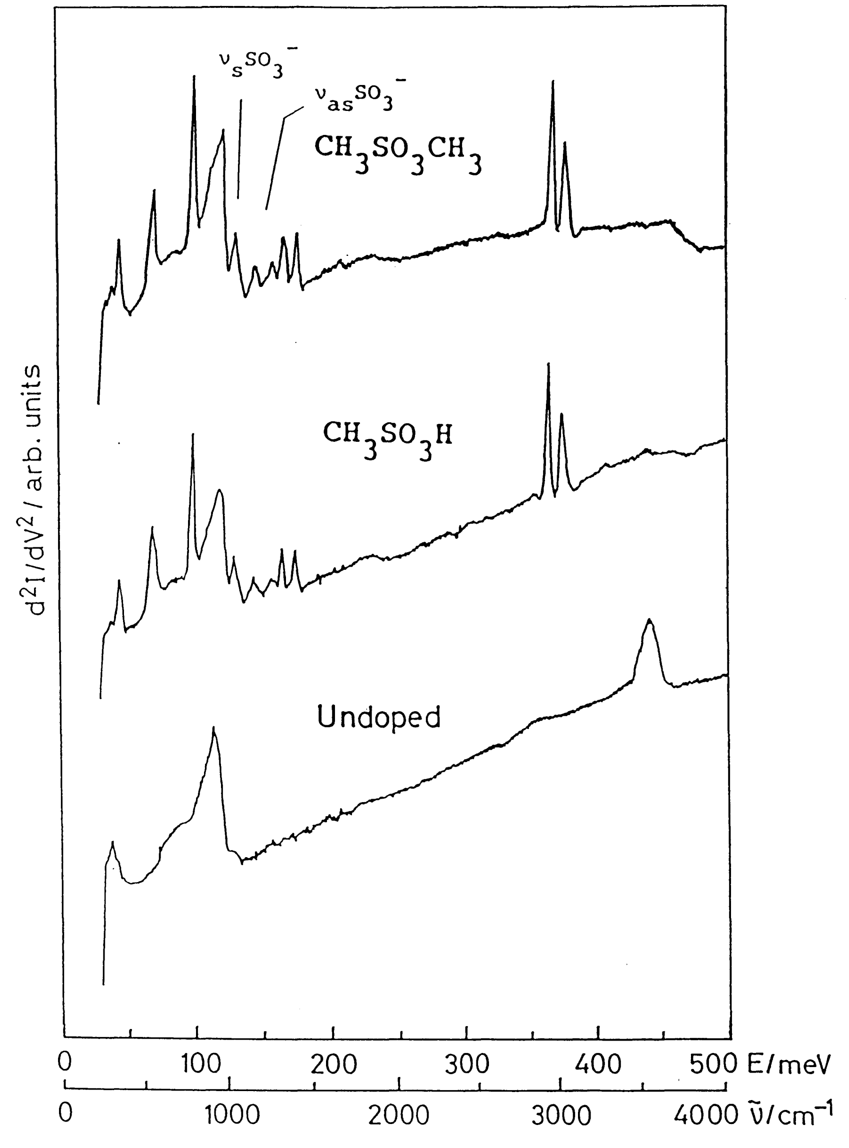

Fig. 1. Tunneling spectra of methyl methanesulfonate and methanesulfonic acid adsorbed onto the alumina surface from benzene solution (1.4 - 2.8 mg/ml). Tunneling spectrum of undoped junction is also shown for comparison.

the vacuum system, and the junction was completed with an evaporated Pb (Wako Chemicals, 99.999%) cross strip(1 mm wide). The resistance for the doped junction was in the range of 50-1000 Ω. The operations were done in a class 10000 clean room(Airtech Japan AER-223C). The tunneling spectra were measured at a liquid-helium temperature(4.2 K). The infrared spectra of methyl sulfonates were measured with Shimadzu FTIR-4200.

The tunneling spectra of adsorbed species for methanesulfonic acid and methyl methanesulfonate onto the Al_2O_3 surface are shown in Fig.1. The tunneling spectrum of methyl methanesulfonate is very similar to that of methanesulfonic acid. In the spectrum of methyl methanesulfonate, the stretching(ν_s, ν_{as}) and deformation(δ_{as}) modes of sulfonate ion are observed at 1039, 1158,and 541 cm^{-1}, respectively. The infrared spectrum of methyl methanesulfonate has strong stretching peaks of ν_sSO_2 and $\nu_{as}SO_2$

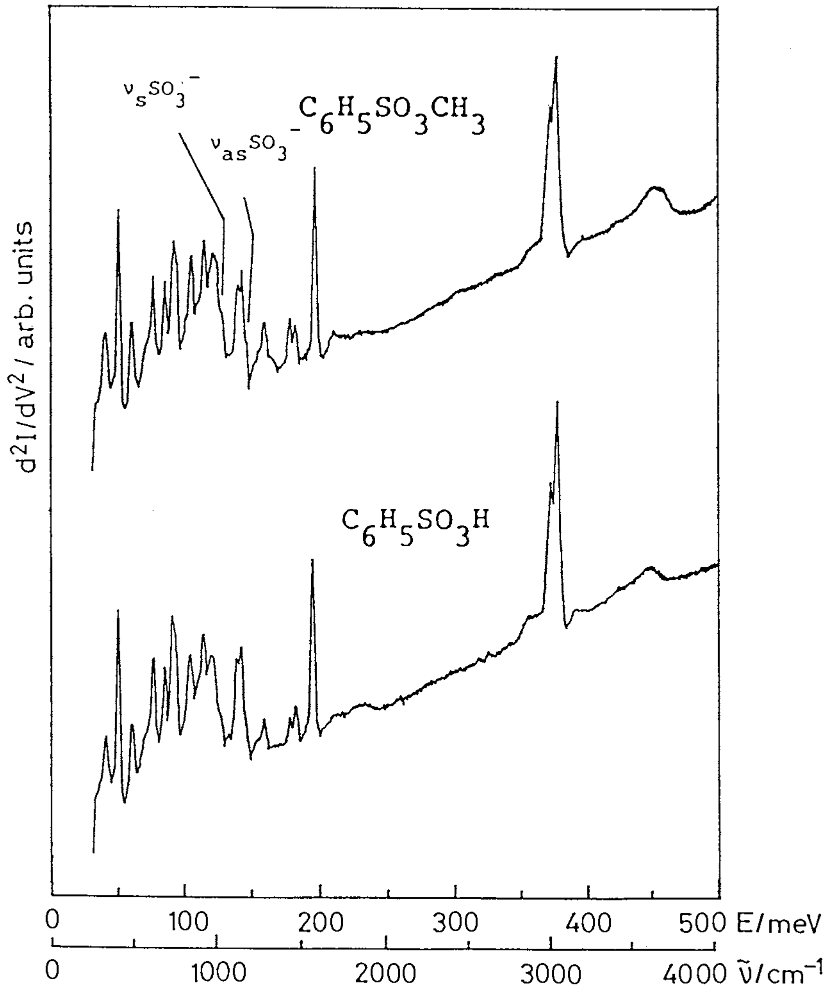

Fig. 2. Tunneling spectra of methyl benzenesulfonate and benzensulfonic acid adsorbed onto alumina surface from benzene solution (1.0 - 3.0 mg/ml).

(1176 and 1348 cm^{-1}), but the tunneling spectrum has no correspoding peaks. The peak intensity of the stretching mode of surface OH groups at around 3620 cm^{-1} are weaker than that of the undoped spectrum. Thus, it is considered that the methyl methanesulfonate reacts with the surface OH group on Al_2O_3 and is adsorbed dissociatively onto the surface as the sulfonated ion.

The tunneling spectra of benzenesulfonic acid and methyl benzenesulfonate onto the Al_2O_3 surface are shown in Fig.2. The tunneling spectrum of the methyl benzenesulfonate has stretching modes of $\nu_s SO_3^-$(1022 cm^{-1}) and $\nu_{as} SO_3^-$(1182 cm^{-1}) and deformation mode of $\delta_{as} SO_3^-$(645 cm^{-1}). Whereas the infrared spectrum of the methyl benzenesulfonate has the peaks of $\nu_s CH_3$(2848 cm^{-1}), $\nu_{as} CH_3$(2960 cm^{-1}), $\delta_s CH_3$(1312 cm^{-1}), $\delta_{as} CH_3$(1448 cm^{-1}) $\nu_s SO_2$(1187 cm^{-1}) and $\nu_{as} SO_2$(1360 cm^{-1}). The tunneling spectrum of the methyl benzenesulfonate, however, has no corresponding peaks. Thus, it can be considered that methyl benzenesulfonate reacts with the surface OH groups of Al_2O_3 to give the adsorbed sulfonate anion and free methanol as in the case of the reaction for methyl methanesulfonate.

The analyses of the vibrational spectra of methyl methanesulfonate and methyle benzenesulfonates indicate that the methyl sulfonates are decomposed by the reaction with surface OH groups of alumina producing sulfonate ions and losing methyl groups to make methanol, and then sulfonate ions are adsorbed perpendicularly on the alumina. Thus we can conclude that the decomposition of the sulfonic esters on alumina has the same reaction as in the case of carboxilic esters$^{2)}$ and phosphites.$^{3,4)}$

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