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ADSORPTION AND ORIENTATION OF TEREPHTHALIC ACID ON ALUMINA OBSERVED BY INELASTIC ELECTRON TUNNELING SPECTROSCOPY

Satuo KAMATA* and Morihide HIGO
Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890

Terephthalic acid adsorbed onto Al_2O_3 from alcohol solution was studied by using inelastic electron tunneling spectroscopy. A comparison with the tunneling spectrum of p-acetylbenzoic acid shows that terephthalic acid is adsorbed predominantly as a monocarboxylate ion onto the alumina surface.

Inelastic electron tunneling spectroscopy (IETS) reveals the vibrational modes of adsorbed species on the oxide of a metal-oxide-metal junction as shown in Fig.1. A vibrational mode of frequency ν appears as a band in the second derivative of the characteristic current-voltage (I-V) function of the junction at cryogenic temperatures (d^2I/dV^2, at a voltage $V=h\nu/e$, where h is Planck's constant and e is the electron charge). The resolution and sensitivity of IETS are sufficient to detect a fraction of a monolayer of the adsorbed species. The useful spectral range extends from 400 to 4000 cm^{-1} and includes all molecular vibrations. Thus, IETS is a powerful analytical technique for investigating the chemical interaction and the structure of species adsorbed onto the oxide surface.$^{1)}$

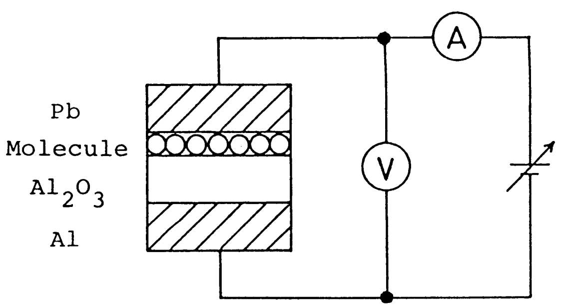

Fig. 1. Schematic representation of the tunneling junction.

Since aluminium oxide is widely used as a catalyst or catalyst support, it is important to know the orientation and structure of adsorbed species for understanding the reaction mechanism on the catalyst. Therefore the investigation of terephthalic acid adsorbed onto Al_2O_3 is interesting and important. Terephthalic acid has two carboxyl groups at the para position. The orientation and structure of this molecule on the alumina surface can be clarified by examining the characteristic C=O band. In this letter, we have reported the adsorption and orientation of terephthalic acid on the alumina surface by comparing its tunneling spectrum with that of p-acetylbenzoic acid.

The method of junction preparation involves evaporation and oxidation techniques in a liquid nitrogen trapped diffusion pumped bell jar. Aluminium (99.999%) was evaporated on a clean glass slide to form three strips (1 mm wide) at a pressure of 10^{-5} Torr (1 Torr = 133.322 Pa). The strips were oxidized by exposure to oxygen (99.8%, 1 atom) in the bell jar.

The slide was removed from the vacuum system, dipped into the alcohol solution containing the sample material, terephthalic (Kanto Chemicals, 99.5%) or p-acetylbenzoic (Aldrich Chemicals) acids, and left for about 3 min. The slide was then returned into the vacuum system, and the junctions were completed with an evaporated Pb (99.999%) cross strip (1 mm wide). The resistance for the doped junction was larger than 50 Ω, while that for the undoped Al-Al_2O_3-Pb junction was smaller than 10 Ω. These operations were made in a class 10000 clean room (Airtech Japan AER-233C).

The diagram of the circuit is shown in Fig. 2. A 500 Hz ac modulation signal of 3.0 - 4.0 mV peak-to-peak from an osillator (NF E-1201) and a slowly varying dc voltage from a bias supply were applied to the junction at liquid-helium temperature (4.2 K). The second harmonic signal was differentially amplified (LM 308AH), and detected with a lock-in amplifier (NF LI-574A), preceded by the bridge circuit developed by Adler and Jackson.[2)]

The tunneling spectrum of benzoic acid was measured using the above device and compared with those results previously reported;[3)] the band positions of the spectrum are in good agreement. The accuracy and resolution of our spectrum were estimated to be ± 0.5 meV (± 4 cm^{-1}) and about 3 meV (≃ 24 cm^{-1}), respectively.

The tunneling spectra of terephthalic and p-acetylbenzoic acids doped with an ethanol solution of 0.5 mg/ml are shown in Fig. 3. Because the tunneling spectrum reveals both infrared and Raman active vibrational modes, the useful information on the adsorbed molecule is given by comparing it with its infrared and Raman spectra.

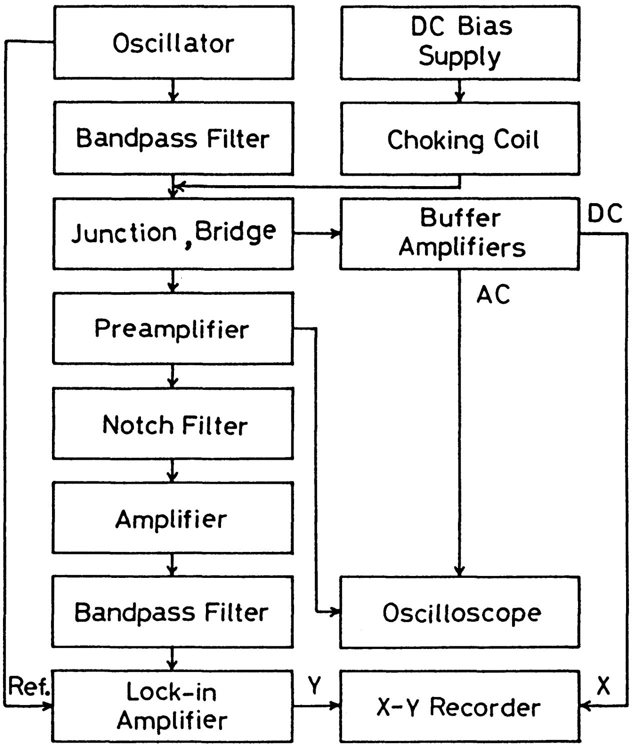

Fig. 2. Diagram of the circuit.

The tunneling spectrum of terephthalic acid has the CH stretching band at 3040 cm^{-1}. The band positions of 1139 and 963 cm^{-1} are assigned to the CH in-plane and out-of-plane bending vibrations. The band positions at 1599, 844, 739, and 681 cm^{-1} are due to the tangential, radial, radial and out-of-plane vibrations of the ring, respectively. Terephthalic acid has a broad OH (2540-2830 cm^{-1}) band owing to hydrogen bonding and a strong C=O (1682 cm^{-1}) band in the infrared spectrum, and also has a very strong C=O (1632 cm^{-1}) band in the Raman spectrum.[4] On the other hand, terephthalate ion has two very strong bands (1380 and 1575 cm^{-1}) based on the COO$^-$ group in the infrared spectrum, and also has very strong (1413 cm^{-1}) and weak

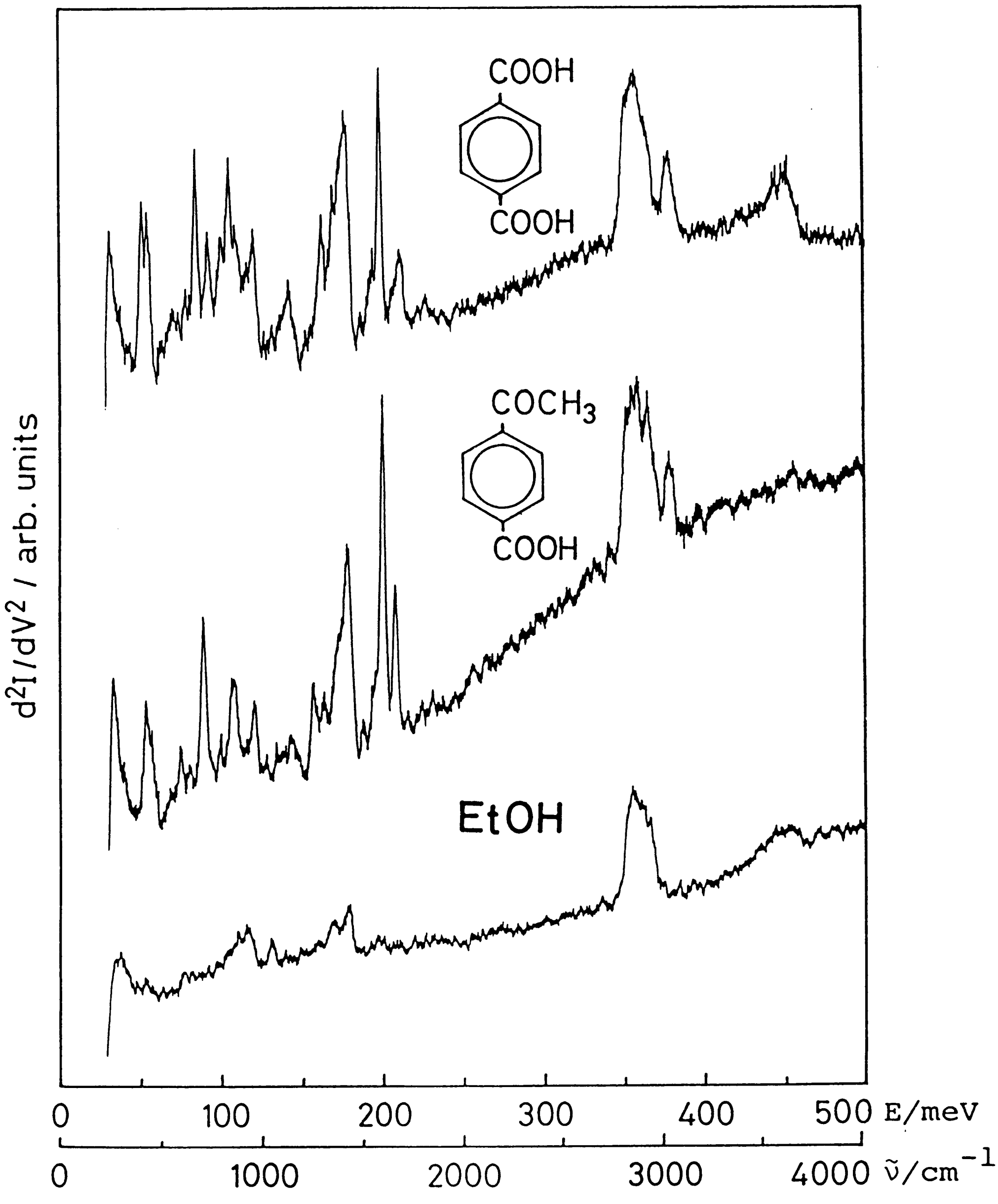

Fig. 3. Tunneling spectra of terephthalic and p-acetylbenzoic acids doped with ethanol solution of 0.5 mg/ml. Tunneling spectrum of ethanol solvent is also shown for a comparison.

(1549 cm^{-1}) bands based on the same group in the Raman spectrum.[5] As can be seen from Fig. 3, the tunneling spectrum of the terephthalic acid has the medium OH (3624 cm^{-1}), medium C=O (1699 cm^{-1}), weak COO^- (1563 cm^{-1}) and strong COO^- (1427 cm^{-1}) band. The fact that the tunneling spectrum has two kinds of bands (the C=O and COO^- bands) points out the presence of the monocarboxylate ion of terephthalic acid on the alumina surface.

The tunneling spectrum of p-acetylbenzoic acid as shown in Fig. 3 has the C=O (1660 cm^{-1}) and the COO^- (1410 cm^{-1}) bands. This means that p-acetylbenzoic acid is adsorbed as the monocarboxylate ion onto Al_2O_3.[6] The relative intensities of the C=O to the COO^- bands in both the tunneling spectra of terephthalic and p-acetylbenzoic acids are similar to each other. This similarity shows that terephthalic acid is adsorbed predominantly as a monocarboxylate ion such as p-acetylbenzoic acid. The tunneling spectra of phthalic and isophthalic acids have strong COO^- and very weak C=O bands. These molecules are found to be adsorbed mainly as dicarboxylate ions onto Al_2O_3.

Oxley et al.[3] have also measured the tunneling spectrum of terephthalic acid doped with water and ethanol solutions onto Al_2O_3 formed by a glow discharge oxidation. Their spectrum, however, has no C=O band and disagrees with ours. We examined the experimental conditions in detail, and found that the tunneling spectrum of terephthalic acid doped with 1-propanol and methanol solutions also has the C=O band. The relative intensity of the C=O band is almost independent of the concentration (0.01-1.5 mg/ml). In the case of methanol solution, however, the relative intensity is somewhat weak. Thus, we conclude that terephthalic acid is adsorbed predominantly as the monocarboxylate ion onto the alumina surface at almost saturation coverage when doped with ethanol and 1-propanol solutions. It seems that this molecule is adsorbed nearly perpendicular to the surface. Judging from the asymmetric tailing of the OH band and the broadness of the C=O band, hydrogen bonding between the adsorbed molecules was obserbed. A similar result has been obtained in the case of p-diphenol in IETS; where hydroquinone is adsorbed predominantly as the monophenolate ion onto the alumina surface.[7] Detailed description of the results and discussion on the isomers of phthalic acid will be presented elsewhere.

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