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Surface Reaction of Dimethyl Phosphite on Alumina and Magnesia Studied by Inelastic Electron Tunneling Spectroscopy

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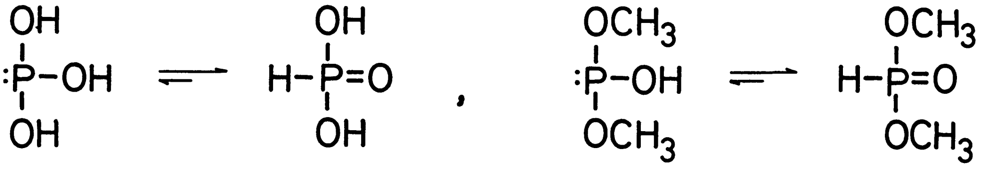
Vibrational spectra of dimethyl phosphite on Al_2O_3 and MgO surfaces have been measured by inelastic electron tunneling spectroscopy. The analysis of the spectra and comparison of the spectrum of phosphorous acid indicate that dimethyl phosphite decomposes on the surfaces and is adsorbed preferentially as the phosphite anion.

Inelastic electron tunneling spectroscopy (IETS) is a unique technique for measuring the vibrational spectrum of adsorbed species on the oxide surface of a metal-oxide-metal tunneling junction at cryogenic temperatures. The high sensitivity and good resolution give the detailed spectrum. The analysis of the spectrum enables us to study not only about the molecular structure on the surface but also about the reaction mechanism on it. The tunneling spectra of many species have been measured and the molecular structures on the surfaces were clarified.1) The tunneling spectra of carboxylic esters showed that these molecules decompose on the Al_2O_3 surfaces to form the adsorbed carboxylate ions.2) Compounds of phosphorus have a variety of molecular structures and chemical properties.3) It is important and interesting to study these compounds on the oxide surfaces. In our previous papers, we have reported the tunneling spectrum of methylphosphonic acid adsorbed on $Al_2O_3$4) and the spectra of diethyl phosphate on Al_2O_3 and MgO5); their molecular structures and the interaction with the surfaces were studied. In this letter, the surface reaction of dimethyl phosphite (O,O-dimethyl phosphonate) on Al_2O_3 and MgO is reported.

The method of junction preparation and the apparatus for measuring the tunneling spectrum have been described in detail elsewhere.6) Aluminium (Mituwa Chemicals, 99.999%) or magnesium (Rare Metallic Co., 99.99%) 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 = 133.322 Pa). The surfaces of the strips were oxidized in an oxygen-dc glow discharge (400 - 800 V, 75 mTorr, 5 mA, 0.5 - 2 min) in the bell jar. Dimethyl phosphite (Nakarai Chemicals, 99.7%), purified twice by vacuum distillation (44.0 - 44.8 °C, 8 mmHg), was adsorbed onto the surfaces from the solution of anhydrous benzene (5 mg/ml) or the vapor (19 Torr, 1 min) in the temperature range 21 - 24 °C. The infrared and Raman spectrum of the dimethyl phosphite were measured and compared with those previously reported.7) Phosphorous acid (phosphonic acid) (Nakarai Chemicals, 99.3%) was adsorbed from the methanol solution (0.5 - 1.0 mg/ml). The junctions were completed with an evaporated Pb (Wako Chemicals, 99.999%) cross strip (1 mm wide). The tunneling spectrum was obtained by measuring the second derivative of the tunneling current through the junction at 4.2 K.

Phosphorous acid (1) and dimethyl phosphite (3) are in tautomeric equilibrium. However, they exist wholly in the structures 2 and 4 because of the high stability of the P=O groups.[3,8]



$$:P(OH)_3 \rightleftharpoons HP(=O)(OH)_2 , \quad :P(OH)(OCH_3)_2 \rightleftharpoons HP(=O)(OCH_3)_2$$

1 2 3 4

The tunneling spectrum of phosphorous acid adsorbed onto the Al_2O_3 surface and the spectra of dimethyl phosphite on Al_2O_3 and MgO are shown in Fig. 1. The spectrum of phosphorous acid shows the very strong stretching (ν) and bending (γ) mode of the PH group at 2440 and 1030 cm^{-1}, respectively. The peaks at 935 and 280 cm^{-1} are due to the vibrational mode of AlO and the aluminium phonon, respectively.[6] There is no peak at around 2900 cm^{-1}, and it shows no contribution of organic contamination and methanol used for the solvent. The spectrum has almost no surface OH peak at around 3600 cm^{-1}. The infrared spectrum of phosphorous acid has the strong νP=O band (1180 cm^{-1}) and the broad νPOH bands (2880 - 2320 cm^{-1}). The tunneling spectrum, however, has no corresponding peaks. Whereas, it shows the weak $\nu_{as}PO_3^{2-}$ peak and the broad deformational ($\delta_s PO_3^{2-}$) peak at 1160 and 560 cm^{-1}, respectively. The $\nu_s PO_3^{2-}$ peak, which exists at 980 - 990 cm^{-1} in the infrared and Raman spectrum of the phosphite anion,[9,10] seems to be involved in the strong νPH peak at 1030 cm^{-1}. Phosphorous acid is found to be adsorbed as the phosphite anion onto the Al_2O_3 surface. It is concluded that phosphorous acid reacts with the surface OH groups of the alumina by loosing the protons of the $PO(OH)_2$ group and is adsorbed as the anion at the Lewis-acid sites on the surface as are the many organic acids.[1] This phosphite anion is considered to be adsorbed almost perpendicularly to the surface in a tripod configuration as in the case of methylphosphonic acid ($CH_3PO(OH)_2$).[4]

The tunneling spectra of dimethyl phosphite on the alumina and magnesia surface also show the strong νPH and γPH peaks at 2370 - 2390 cm^{-1} and 1005 cm^{-1}, respectively. The spectra have the $\nu_{as}CH_3$, $\nu_s CH_3$, $\delta_s CH_3$, γCH_3 peaks at 2970, 2825, 1440, 1180 cm^{-1}, respectively. The medium peaks at 800 cm^{-1} are due to the νP-O- mode. The surface OH groups (ca. 3600 cm^{-1}) are somewhat present on both the oxides. Although the molecular structure of dimethyl phosphite is different from that of phosphorous acid, the features of the spectra of dimethyl phosphite are similar to those of the spectrum of phosphorous acid. The infrared and Raman spectrum of dimethyl phosphite have the strong νP=O band (1250 - 1280 cm^{-1}) and the medium $\nu(C\text{-}O)_2$ bands (1040 - 1080 cm^{-1}).[7] The tunneling spectra on both the surfaces, however, have no corresponding peaks. On the other hand, the tunneling spectra show the peaks owing to the $\nu_{as}PO_3^{2-}$ and/or $\nu_{as}PO_2^{-}$ and $\delta_s PO_3^{2-}$ and/or

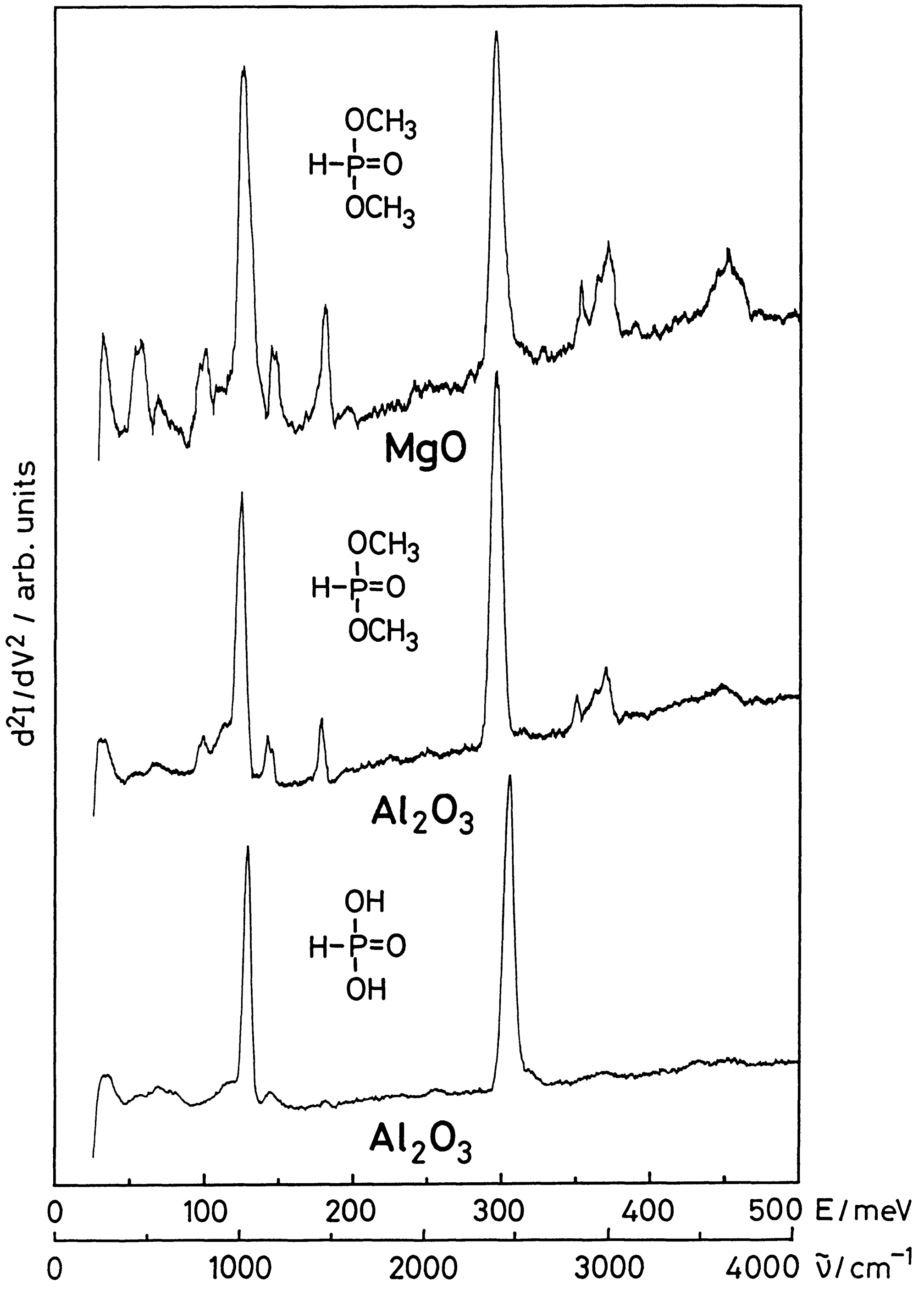


Fig. 1. Tunneling spectra of dimethyl phosphite adsorbed onto the alumina and magnesia surface from an anhydrous benzene solution (5 mg/ml) and the spectrum of phosphorous acid on the alumina surface from a methanol solution (1 mg/ml). These spectra show the very strong νPH (2370 - 2440 cm^{-1}) and γPH (1005 - 1030 cm^{-1}) peaks. Phosphorous acid is adsorbed as the phosphite anion onto the Al_2O_3 surface. The similarity of the spectrum of dimethyl phosphite and phosphorous acid indicates that dimethyl phosphite decomposes on the surfaces and is adsorbed preferentially as the phosphite anion.

$\delta_s PO_2^-$ mode at 1150 - 1160 cm^{-1} and about 550 cm^{-1}, respectively. The $\nu_s PO_3^{2-}$ ($\nu_s PO_2^-$) peaks also seem to be involved in the strong γPH peaks at 1005 cm^{-1}. The $\nu_s PO_2^-$ peak in the case of diethyl phosphate, $(C_2H_5O)_2PO(OH)$, adsorbed onto the Al_2O_3 and MgO surface exists at 1092 and 1096 cm^{-1}, respectively.$^{5)}$

Although dimethyl phosphite has no dissociative $PO(OH)_2$ (PO(OH)) group, the presence of the PO_3^{2-} and/or PO_2^- group and the similarity of the features of both the tunneling spectra of dimethyl phosphite and phosphorous acid indicate that dimethyl phosphite is adsorbed onto the Al_2O_3 and MgO surface in a similar molecular structure as that of phosphorous acid. Bayman et al.$^{2)}$ have studied the decomposition of carboxylic esters on Al_2O_3 by IEST; their tunneling spectra of carboxylic esters closely resemble those of the corresponding carboxylic acids. They concluded that carboxylic esters react with the surface OH groups to form the adsorbed carboxylate anions and free alcohol molecules which are pumped away. Dimethyl phosphite has two P-O-C bonds of phosphonate ester and, thus, it is expected that these bonds dissociate in a similar mechanism as that of carboxylic esters.$^{11)}$ Therefore, it can be concluded that dimethyl phosphite reacts with the surface OH groups on Al_2O_3 and MgO and gives preferentially the adsorbed phosphite anion and free methanol molecules. However, the CH_3 peaks and the νP-O- peaks in the spectra of dimethyl phosphite may indicate the presence of monomethyl phosphite anion, $(CH_3O)(H)PO_2^-$, on the surfaces. A similar result has been obtained in the case of phosphonate esters on Al_2O_3; Templeton and Weinberg$^{12)}$ have reported decomposition of dimethyl methylphosphonate, $(CH_3O)_2(CH_3)PO$, by IETS.

Further investigations on other compounds of phosphorus are now in progress.

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