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Adsorption of Diethyl Phosphate on Alumina and Magnesia Surface Studied by Inelastic Electron Tunneling Spectroscopy

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Inelastic electron tunneling spectroscopy has been used for obtaining the vibrational spectra of diethyl phosphate adsorbed onto the alumina and magnesia surfaces. The analysis of the spectra and comparison of the infrared and Raman spectra show that the diethyl phosphate is adsorbed as the anion onto both the oxide surfaces.

Inelastic electron tunneling spectroscopy (IETS) is a unique technique using the tunneling phenomena of electrons through a metal-oxide-metal junction at cryogenic temperatures. The high sensitivity, resolution and wide spectral range enable us to obtain the detailed vibrational spectrum of the adsorbed species on the oxide surface. The tunneling spectra of carboxylic acids,[1] sulfonic acids,[2] and phosphonic acid[3] have been measured; these acids are found to be adsorbed as the anions onto the surfaces. In this letter, we report for the first time the spectra of diethyl phosphate adsorbed onto the alumina and magnesia surfaces.

The junction was prepared by the evaporation and oxidation technique in a bell jar of a vacuum evaporator. The details have been described before.[4] Diethyl phosphate (Kanto Chemicals, 98%) was adsorbed onto the surfaces from a benzene, methanol or aqueous solution. The tunneling spectra were measured at 4.2 K.

The spectra of diethyl phosphate adsorbed onto the Al_2O_3 and MgO surface show the very strong peaks due to the stretching modes of CH at about 2950 and 2910 cm^{-1} (Fig. 1). The peaks at 1465 - 1160 cm^{-1} of both the spectra are owing to the deformational modes of the CH_3 and CH_2 groups. The peaks at around 1040 cm^{-1} are caused by the νCO mode. The peaks at 960 and 810 cm^{-1} are due to the νCC mode and the $\nu_{as}P(-OC)_2$ mode, respectively. The $\nu_sP(-OC)_2$ mode (ca.760 cm^{-1}) appears as the shoulder in the Al_2O_3 spectrum, whereas it appears as the peak in the MgO spectrum. The infrared spectrum of diethyl phosphate has a medium νP=O band (1240 cm^{-1}) and broad νOH bands (2690 - 2160 cm^{-1}). However, both the tunneling spectra have no corresponding peaks. Whereas, the spectrum on Al_2O_3 and MgO has the $\nu_sPO_2^-$ peak at 1092 and 1096 cm^{-1}, respectively. These peak positions agreed with those of the infrared (1092 cm^{-1}) and Raman (1101 cm^{-1}) spectrum of the phosphate ion.[5] Diethyl phosphate is clarified to be adsorbed as the anion onto the Al_2O_3 and MgO surface as are the organic acids.[1-3] It is concluded that diethyl phosphate reacts with the surface OH group of both the oxides by loosing the proton of the PO_2H group and is adsorbed as the anion at the Lewis-acid site (Al^+, Mg^+) on the surface.

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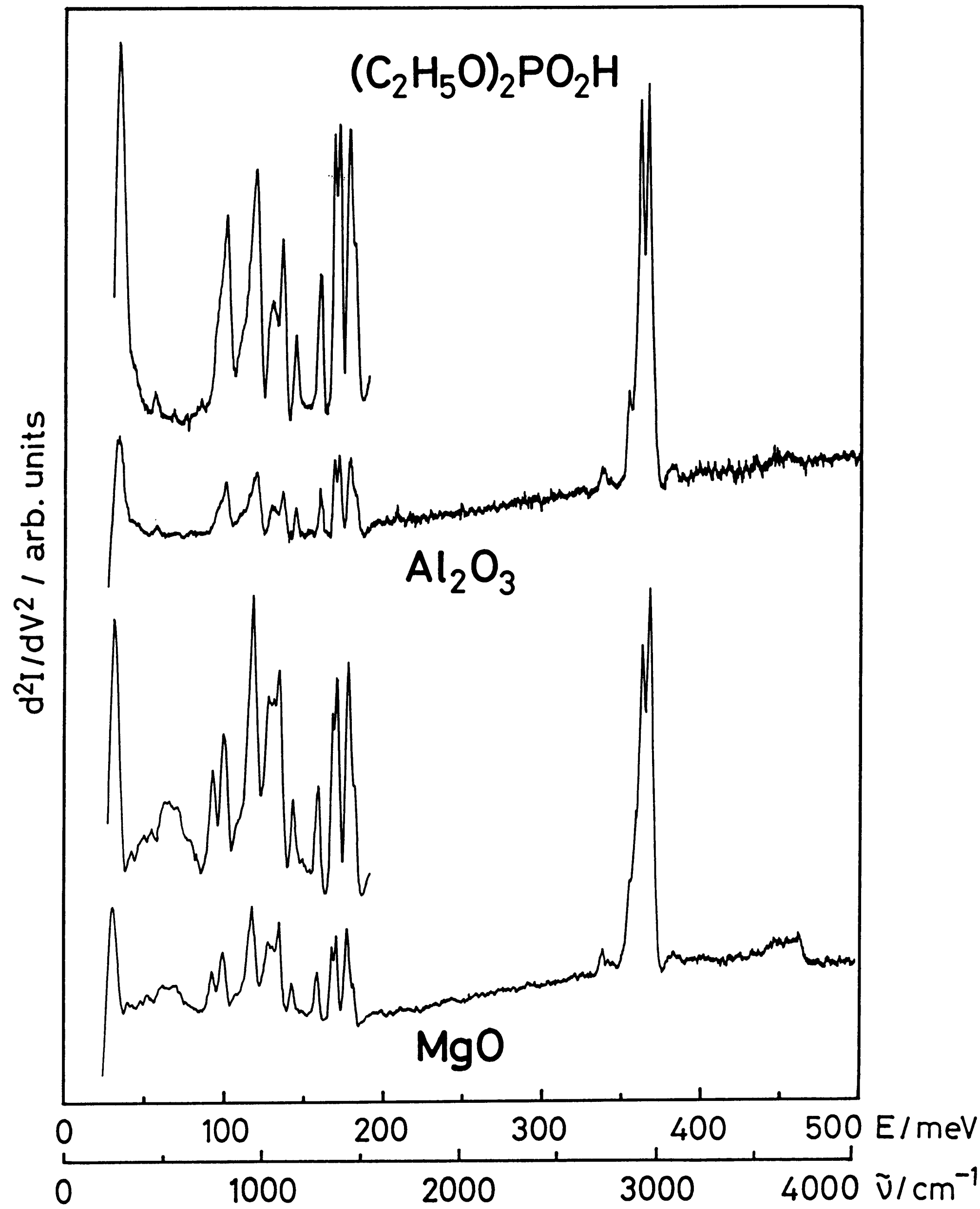

Fig. 1. Tunneling spectra of diethyl phosphate adsorbed onto the alumina and magnesia surface from benzene solutions (0.1 - 0.6 mg/ml). The expansions of the ordinates of the lower frequency regions (<1500 cm^{-1}) are also shown.

References

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