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Reduction of Nitrobenzenes on Thin Aluminium Oxide Utilized in Inelastic Electron Tunneling Spectroscopy

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Chemical interactions between aromatic nitro compounds and thin aluminium oxide grown on aluminium film were studied by the combined use of inelastic electron tunneling spectroscopy (IETS) and X-ray photoelectron spectroscopy (XPS). IET spectra of nitrobenzoic acids and nitrophenols show that nitro groups of these compounds are reduced on the oxide and result in the corresponding amino compounds. In this conversion reaction, oxygen atoms of nitro group are consumed for the growth of the oxide layer and hydrogen atoms of the surface hydroxyl groups are used for the amidation reaction. The intermediate of the reaction is identified to the corresponding nitroso compounds from the XPS analysis.

Inelastic electron tunneling spectroscopy (IETS) is a useful technique to obtain a vibrational spectrum of trace amounts of chemical species adsorbed on aluminium oxide. In certain cases, vibrational spectra obtained by IETS partly differ from IR or Raman spectra of parent molecules. This is induced by chemical interaction between the sample molecules and aluminium oxide surface. Therefore the elucidation of the mechanism for the interactions between various samples and aluminium oxide surface is the present interest, in order to establish IETS as a useful analytical tool. The major chemicals whose IET spectra have been investigated are carboxylic acids,1–4) alcohols,5,6) amines,7,8) sulfonic acids,9) phenols,10) unsaturated hydrocarbons,11) and esters.12)

Tremendous difference is found in the molecular vibrational spectra of nitro compounds between IETS and IR spectroscopy and we focussed a study on the isomers of nitrobenzoic acids and nitrophenols. The interactions between these aromatic nitro compounds and aluminium oxide surface are observed by both methods of IETS and X-ray photoelectron spectroscopy (XPS). We chose to study mainly on *p*-nitrobenzoic acid (PNBA), because the vibrational spectra of adsorbed PNBA on various substrates have been measured by other spectroscopic techniques such as surface enhanced Raman scattering,13–15) surface picosecond Raman gain16) and Fourier transform infrared emission spectroscopy.17)

Experimental

The sample-loaded tunneling junctions for IETS measurements were prepared using procedures as described elsewhere.18) Briefly, the aluminium oxide layer was formed on a vacuum deposited aluminium film (*ca.* 300 nm thick) by exposing the film to atmospheric pressure of oxygen containing H_2O or D_2O vapor for 5 min. Samples were then loaded with 0.1 and 1 mg cm^{-3} acetone solutions. Tunnel junctions of Al–AlO_x–sample–Pb sandwich structure were completed by depositing the top lead electrode (*ca.* 300 nm thick).

Usually, for single ring compounds, IET spectra were successfully obtained from 1 mm×1 mm junctions. In the case of nitrobenzene derivatives, however, 2 mm×3 mm junctions were employed to obtain the spectra of sufficient quality. Because the junctions loaded with nitrobenzene derivatives showed large resistance and junctions of large resistance result in the spectra of poor signal to noise ratio. IET spectra were recorded at 4.2 K with a modulation voltage of 1.2 mV rms using the circuit described previously.18) The observed peak positions were converted from millivolt to wavenumber with correlation of 1 mV=8.065 cm^{-1}. And a correction of -7 cm^{-1} was made to cancel out the superconducting energy gap of lead electrode.

X-ray photoelectron spectra were measured at room temperature on a Shimadzu Hips-70 spectrometer with Mg *Kα* radiation. In XPS measurement, samples were prepared in a similar manner as above but without lead top electrode. Loaded samples were washed with fresh acetone to remove multilayer physisorbed sample molecules. Binding energy of Al2p(metal) peak was taken to be 72.8 eV19) and used as the energy standard.

Chemicals used were obtained from Wako Pure Chemical Ind. or Nakarai Chemical Co. They were recrystallized from water, ethanol or toluene before use. D_2O(99.85%) for preparing deuterated oxide, was purchased from Commissariat a l'Enerqie Atomique.

Results and Discussion

IET Spectra. IET spectrum of PNBA adsorbed on aluminium oxide is shown in Fig. 1-A. Since there observed a peak due to the symmetric stretching mode of carboxylato group at 1424 cm^{-1}, PNBA is considered to be adsorbed on the oxide by dissociating a proton of carboxyl group to form surface carboxylate. In the IET spectrum of PNBA, the most remarkable feature is that the peaks attributed to the vibrational modes of nitro substituent are all absent. Instead, there appear unexpected peaks for PNBA at 3340 cm^{-1} and at 3445 cm^{-1}. These peaks could be assigned to the symmetric and antisymmetric stretching modes of amino group respectively. Further, twisting mode of amino group is observed at 1058 cm^{-1}. This spectrum is essentially identical to the IET spectrum of *p*-aminobenzoic acid (PABA) shown in Fig. 1-B. The observed peak positions and their tentative assignments are listed in Table 1.

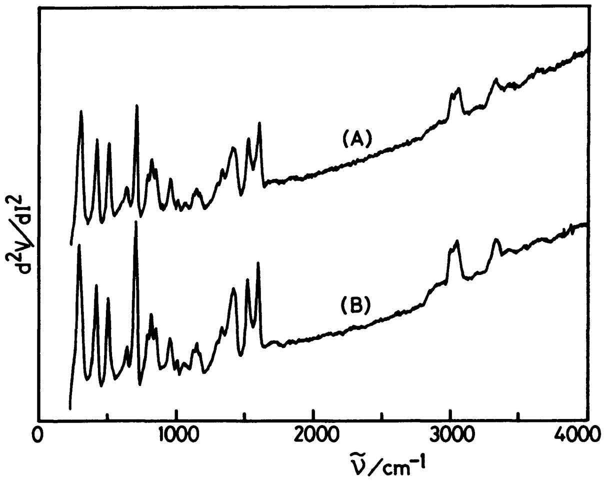

Fig. 1. IET spectra of *p*-nitrobenzoic acid(A) and *p*-aminobenzoic acid(B) adsorbed on aluminium oxide.

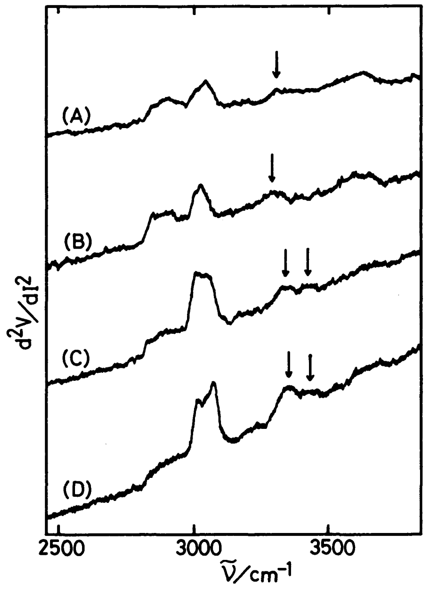

Fig. 2. Expanded IET spectra of *p*-nitrophenol(A), *o*-nitrophenol(B), *m*-nitrobenzoic acid(C) and *p*-nitrobenzoic acid(D) on aluminium oxide. Peaks due to N–H stretching modes are indicated by arrows.

TABLE 1. IET SPECTRAL DATA OF *p*-NITROBENZOIC ACID AND *p*-AMINOBENZOIC ACID ON ALUMINIUM OXIDE

Peak position[a]/cm^{-1}			Approximate description[b]
PABA	PNBA	PNBA on deuterated oxide	
3638 w-b	3638 w-b		ν(OH)
3445 w-b	3445 w-b		$\nu_a(NH_2)$
		3380 w-b	ν(NHD)
3342 m-b	3340 m-b		$\nu_s(NH_2)$
3060 m	3060 m	3061 m	ν(CH)
3009 m	3007 m	3009 m	ν(CH)
		2687 w-b	ν(OD)
		2570 w-b	$\nu_a(ND_2)$
		2496 w-b	ν(NHD)
		2429 m-b	$\nu_s(ND_2)$
1605 s	1604 s	1605 s	ν(CC)
1528 s	1527 s	1527 s	ν(CC)
1421 s-b	1424 s-b	1425 s-b	ν(CC), ν_s(COO)
1342 w	1337 w		?
1307 w	1304 w	1318 w	β(CH)
1182 w	1180 w	1180 w	X-sens.
1158 w	1157 w	1150 w	β(CH)
1129 w	1129 w	1116 w	β(CH), X-sens.
1061 w-b	1058 w-b		twist(NH_2)
1012 w	1011 w	1011 w	β(CH)
958 w-b	958 w-b	958 w-b	γ(CH)
852 m	851 m	852 m	γ(CH), δ(COO)
818 m	818 m	818 m	γ(CH), X-sens.
		796 m	twist(ND_2)
791 m	788 m		X-sens.
704 vs	705 vs	704 vs	ϕ(CC)
640 w	639 w	639 w	α(CCC)
616 sh	614 sh	610 sh	X-sens.
505 s	504 s	507 s	ϕ(CC)
417 s	416 s	417 s	ϕ(CC), X-sens.
296 vs	295 vs	293 vs	X-sens.

a) Peak positions corrected as in the text, relative intensity also shown; s=strong, m=medium, w=weak, v=very, sh=shoulder, b=broad. b) Assignment based on IR and Raman spectra of *p*-disubstituted benzenes; Ref. 29, alkali metal benzoate; Ref. 30 and anilines; Ref. 31.

These facts indicate that nitro group of PNBA is converted to amino group on the oxide, and PNBA and PABA give same adsorbed species. The similarity of the IET spectrum of PNBA to that of PABA has been suggested by Tsang *et al.*[15] But detailed analysis of the spectra and the conversion reaction was not cited in their study. Korman and Coleman[20] have also studied the IET spectrum of PNBA and assigned the peaks at 1343 cm^{-1} and at 1532 cm^{-1} to the symmetric and antisymmetric stretching modes of nitro group (in our observation 1337 cm^{-1} and 1527 cm^{-1}). However, these peaks are also observed in the IET spectrum of PABA. Thus these peaks should be assigned to the ring modes or modes of amino group and not to the modes of nitro group.

In the IET spectra of other nitrobenzene derivatives also there observed the peaks due to N–H stretching modes instead of the peaks corresponding to nitro substituent. Figure 2 shows the expanded IET spectra of several nitro compounds in 2500 to 4000 cm^{-1} region. In each spectrum, one or two peaks corresponding to N–H stretching modes are observed around 3300 cm^{-1} as disignated in arrows. Therefore the conversion reaction on the aluminium oxide is thought to be common for aromatic nitro compounds.

XPS Spectra. In order to obtain an IET spectrum, lead metal must be deposited on the sample as a counter electrode. To investigate the effect of the lead cover electrode for the conversion reaction, X-ray photoelectron spectra were measured on the similar system discussed above without lead electrode.

Figure 3 shows Nls photoelectron spectra of PNBA and PABA on the aluminium oxide. As the spectrum of PNBA changed with the time-course, spectra were recorded at regular time interval. In the spectrum of PNBA immediately after loading (Fig. 3-a), there observed two peaks at 406.9 eV and at 401.6 eV. With the elapse of time, the relative intensity of the two peaks reverses and the low energy peak is shifted to lower binding energy. But the total intensity of the two peaks is kept constant. One hundred minutes after loading (Fig. 3-f), the peak at 406.9 eV is completely missing and only single peak at 400.6 eV is observed in the spectrum. The resultant spectrum well agrees with that of PABA on the oxide (Fig. 3-g).

The peak at 406.9 eV is considered to be attributed to nitro group and the peak at 400.6 eV is to be due to amino group from analogy with the XPS results[21,22] of nitrobenzenes and anilines. Therefore it is clear that the conversion reaction of nitro to amino group takes place without lead cover electrode and the conversion proceeds rather slowly after adsorption reaction.

The peak at 401.6 eV initially appears in the spectrum is considered to be transient intermediate. It is known that nitrosobenzene radical is produced as an intermediate species of electrochemical reduction of nitrobenzene.[23] And the observed binding energy is in good agreement with that of nitrosobenzene in solid state.[22,24] Thus the intermediate is considered to be nitrosobenzoate on the oxide. However, we cannot rule out the possibility of phenyl-hydroxyl amine like species as an intermediate, because this species is also proposed as an intermediate of the reduction of nitrobenzene.[25]

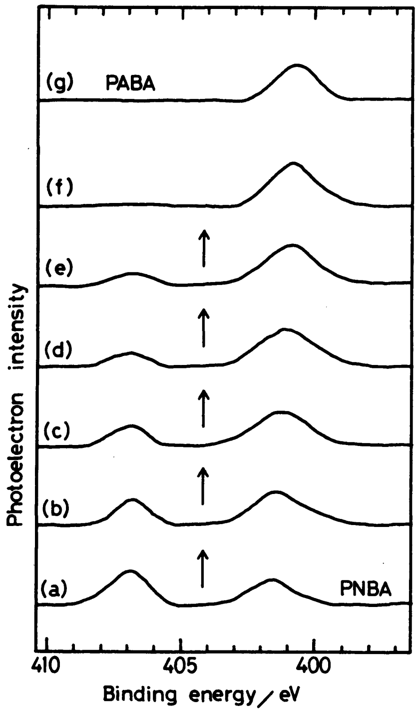

Fig. 3. Nls photoelectron spectra of PNBA on aluminium oxide measured 10 min(a), 25 min(b), 40 min(c), 55 min(d), 70 min(e), and 100 min(f) after loading, and that of PABA(g) on aluminium oxide.

Analysis of the Conversion Reaction. Although PNBA and PABA give the same adsorbed species on the oxide and the obtained IET spectra show similar intensities (indicating that the surface concentration of both compounds is comparable), the tunneling resistance of the junction loaded with PNBA is about 10 times that of the junction with PABA. This difference in tunnel resistance is considered to reflect the difference in the thickness of the insulating oxide layer. To obtain more precise information, the thickness of the oxide layer has been calculated from the XPS data as follows.

Figure 4 shows the schematic view of the surface layers of aluminium–aluminium oxide-adsorbate system and its XPS Al2p spectrum. By assuming that the oxide and the adsorbate layers are uniform, the Al2p photoelectron intensity from the metal substrate, I_m, can be expressed by

$$I_m = I_m^0 \exp(-d/\lambda_o \sin\theta)\exp(-l/\lambda_a \sin\theta), \qquad (1)$$

where I_m^0 is the Al2p photoelectron intensity of the clean aluminium metal film, d is the thickness of the oxide layer, λ_o is the electron mean free path value in the oxide layer for the Al2p metal peak, θ is the photoelectron collection angle with respect to the sample plane, l is the thickness of the adsorbate layer and λ_a is the electron mean free path value in the adsorbate for the Al2p metal peak. As the kinetic energy of electrons for Al2p metal peak is nearly equal to that for Al2p oxide peak, the mean free path values for the two peaks are considered to be equal. Thus the intensity of the photoelectron from the oxide layer I_o can be expressed

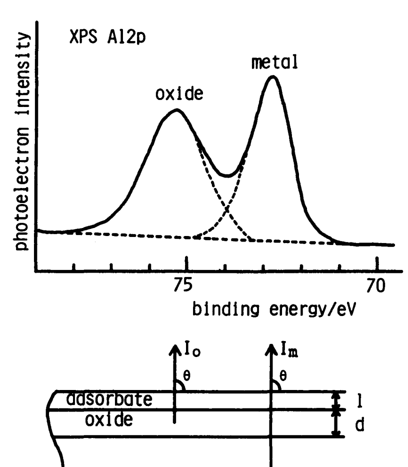

Fig. 4. Schematic view of surface layers and XPS Al2p spectrum.

TABLE 2. RESISTANCE OF TUNNEL JUNCTION AND THICKNESS OF THE OXIDE FOR VARIOUS TREATMENT

	Wet O_2 5 min (A)	(A) + acetone	(A) + PABA	(A) + PNBA
Junction resistance[a)]/Ω	0—5	0—10	100—450	1400—8000
Oxide thickness[b)]/nm	1.26±0.07	1.31±0.04	1.34±0.05	1.59±0.08

a) Resistance of 1 mm × 1 mm junction. b) Estimated from XPS A12 p metal to oxide intensity ratio, see text.

as

$$I_o = I_o^0[1-\exp(-d/\lambda_o \sin\theta)] \exp(-l/\lambda_a \sin\theta), \tag{2}$$

where I_o^0 is the photoelectron intensity of the thick oxide layer without covering layer. By dividing Eq. 1 by Eq. 2, the terms including the effects of the adsorbate layer can be cancelled out and we obtain an equation:

$$\frac{I_m}{I_o} = \frac{I_m^0 \exp(-d/\lambda_o \sin\theta)}{I_o^0[1-\exp(-d/\lambda_o \sin\theta)]}. \tag{3}$$

Thus the thickness of the oxide layer, *d*, is given by

$$d = \lambda_o \sin\theta \ln[1+(I_m^0/I_o^0)(I_o/I_m)]. \tag{4}$$

In the present experiment, $\theta=\pi/2$ and the observed value of I_m^0/I_o^0 is 1.33 for Al2p photoelectron. And with assuming λ_o=1.50 nm for about 1180 eV kinetic energy electron,[26)] the thickness of the oxide layer in nm can be expressed by

$$d = 1.50 \ln[1+1.33(I_o/I_m)]. \tag{5}$$

With Eq. 5, the thickness of the oxide layer can be estimated from the Al2p photoelectron intensity ratio, I_o/I_m, even if the surface is covered with unknown amounts of adsorbates.

In Table 2, junction resistance and estimated oxide thickness for various treatment are listed. The oxide thickness is little affected by the adsorption of PABA, while the adsorption of PNBA causes apparent enlargement of the thickness. This is also revealed in the difference of tunneling resistance. These facts imply that the conversion reaction results in the increase of the oxide thickness. Thus it is clear that the oxygen atoms of the nitro group are consumed for the growth of the oxide layer with conversion reaction.

The hydrogen required for the conversion is thought to be present on the substrate surface as hydroxyl group. If surface hydroxyl groups are deuterated, we can elucidate the mechanism of the conversion reaction. Figure 5 shows the expanded IET spectrum of PNBA on the oxide grown with oxygen containing D_2O vapor. Treatment with D_2O is expected to give the surface OD group. The observed peak positions are listed in Table 1. In the spectrum, characteristic peaks due to N-D stretcing modes are observed at 2500 cm^{-1} region. This observation indicates that the hydrogen atom or the surface hydroxyl group is used for the conversion reaction of nitro to amino group. The small peak at 3380 cm^{-1} is thought to appear by the reaction with residual surface OH group to form -NHD species.

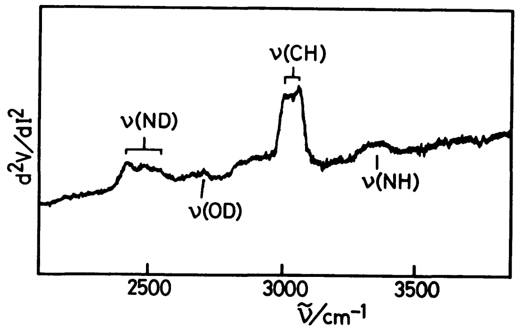

Fig. 5. Expanded IET spectrum of *p*-nitrobenzoic acid adsorbed on deuterated aluminium oxide.

On bulk alumina, it is concluded from ESR study[27)] that nitrobenzene and their derivatives were adsorbed as anion radicals, and the conversion of nitro group to amino group has not been reported. Thus the conversion is thought to be specific reaction on the oxide utilized for IETS. This phenomena can be explained as follows. The oxide formed on aluminium metal is known to reach a limiting thickness of 4.5 nm after one month in air,[28)] whereas the thickness of the oxide layer utilized for IETS is only *ca.* 1.3 nm (Table 2). So the oxide layer can easily grow by the reaction with oxidizing chemicals (in this case, nitro substituent). In the case of bulk alumina, this reaction cannot take place.

In previous paper,[18)] we indicated that the oxide surface used in IETS behaves as base (OH donor) against acidic functional group such as -COOH, -OH, and -SH. In the case of conversion reaction reported here, however the surface hydroxyl group acts as hydrogen donor. Thus the oxide surface exhibits various properties in accordance with the property of the adsorbate and the reactivity is quite different from bulk alumina.

From the results obtained by this study, it is found that IETS cannot be used to distinguish between nitro group and amino group. It is a serious problem to apply IETS to the identification of unknown compounds containing amino or nitro group. Further studies on the property of the oxide used in IETS and the modification of the oxide are needed in order to solve this problem.

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