Orientation of Isomeric Phthalic Acids on Alumina and Magnesia Surface Observed by Inelastic Electron Tunneling Spectroscopy

Morihide HIGO,* Sinichi MIZUTARU,† and Satsuo KAMATA
Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890

(Received November 4, 1988)

The vibrational spectra of phthalic, isophthalic, and terephthalic acid adsorbed onto alumina and magnesia surfaces from the gas phase have been measured by inelastic electron tunneling spectroscopy. The analysis of the tunneling spectra shows that phthalic and isophthalic acid react with the surface OH groups on Al_2O_3 and MgO to give the adsorbed dicarboxylate ions on both surfaces. Phthalic acid is adsorbed with its benzene ring perpendicular to the surfaces, while isophthalic acid is adsorbed parallel to the surfaces. However, terephthalic acid is adsorbed predominantly as the monocarboxylate ion almost perpendicular to the alumina surface, while it is adsorbed as the dicarboxylate ion parallel to the magnesia surface. These results suggest the different properties of the surface OH groups on Al_2O_3 and MgO. There are more than one type of OH group on the alumina surface and they interact with each other through hydrogen bonding. The magnesia surface has an isolated and a hydrogen-bonding OH group. The OH groups on MgO are more basic than those on Al_2O_3, and thus have higher reactivity. The different properties and basicity of the OH groups cause the different orientation and reactivity of the adsorbed terephthalic acid on the alumina and magnesia surfaces.

Recently there has been an increased interest in a new technique for investigating a metal surface and adsorbed species on it. Inelastic electron tunneling spectroscopy (IETS) is a relatively new and a unique technique using the phenomena of electron tunneling through a metal-oxide-metal tunneling junction at cryogenic temperatures. It reveals the vibrational spectrum of the oxide surface and the adsorbed species on it. The high sensitivity and wide spectral range inherent in IETS enable us to analyze the surface and the adsorbed species in detail.[1)]

Alumina has been widely used as the oxide of the tunneling junction for its chemical, physical, and electric stability, in addition to its ease of formation.[1–3)] Few IETS studies, however, have utilized magnesia.[4–14)] The surfaces of alumina and magnesia have been studied by infrared spectroscopy,[15–17)] and their surface models have been proposed.[18–20)] These oxides are used as catalysts or catalyst supports in chemical engineering. Alumina is an amphoteric oxide and magnesia is a basic one; thus, these oxides have interesting and sometimes different catalytic properties. However, their surface states and their chemical interaction with adsorbed species are not well understood.[21,22)] Thus, the measurement and analysis of the tunneling spectra of Al_2O_3 and MgO and the adsorbed species on both surfaces are important and interesting.

The isomeric phthalic acids have two carboxyl groups bonded to a single benzene ring. The important information on their structures and orientations on oxide surfaces can be obtained by examining the characteristic C=O group. Oxley et al.[23)] measured the tunneling spectra of the isomeric phthalic acids on Al_2O_3. They reported that these acids are adsorbed as the dicarboxylate ions. In our previous papers,[24,25)] however, we have shown that phthalic and isophthalic acid are adsorbed as the dicarboxylate ions, while terephthalic acid is adsorbed predominantly as the monocarboxylate ion onto Al_2O_3. Lewis and Field[26)] also measured the tunneling spectra of these acids on Al_2O_3, however, they reported that these acids are adsorbed as the monocarboxylate ions. The geometry of the isomeric phthalic acids on colloidal silver particles was studied by surface-enhanced Raman spectroscopy.[27)] Adsorption of terephthalic acid and terephthalic-d_4 acid onto alumina surfaces has been investigated by external reflection infrared spectroscopy.[28)]

In this study, the tunneling spectra of the isomeric phthalic acids adsorbed onto Al_2O_3 and MgO from the gas phase have been obtained. The analysis and comparison of these spectra and the tunneling spectra of isomeric phthalic acids adsorbed onto Al_2O_3 from alcohol solutions clarify the discrepancy of the previous results. These results also give important information on the properties of both surfaces and the chemical interaction with the adsorbed species. The properties of the alumina and magnesia surfaces, and the orientation and reactivity of the isomeric phthalic acids on both surfaces are discussed.

Experimental

The junctions were prepared in a bell jar of a vacuum evaporator evacuated with a liquid nitrogen-trapped 4-inch diffusion pump (ANELVA CDP-600A). The pressure in the bell jar was measured with an ionization gauge (DAIA VACUUM IT-10P) or a Pirani gauge (DAIA VACUUM PT-9P).The base pressure was 6×10^{-7} Torr (1 Torr=133.322 Pa).

Aluminium (Mituwa Chemicals, 99.999%) or magnesium (Rare Metallic Co., 99.99%) was evaporated from a resistively heated molybdenum boat onto a clean glass slide (13×37×1 mm) to form three strips (1 mm wide) at a pressure of 10^{-6} Torr. Magnesium was evaporated from a molybdenum boat with a cover which has a slit in order to prevent the

---

[†] Present address: Toshiba Electronic Device Engineering Co., 72, Horikawa-chou, Saiwai-ku, Kawasaki 210.

dispersion of the chips from the boat. The surfaces of the strips were oxidized in an oxygen-DC glow discharge (400—800 V, 75 mTorr, 5 mA, 15—30 s) in the bell jar. For the undoped alumina and magnesia junctions, the longer oxidation time of 1.5—2 and 8—10 min was used, respectively.

The sample molecules were adsorbed onto the oxide surfaces from the gas phase (60—320 mTorr, 60 min) by evaporating the acid from a molybdenum boat at 80—100 °C in the bell jar. Phthalic, isophthalic, and terephthalic acid (Kanto Chemicals, >99.5%) and *p*-acetylbenzoic acid (Aldrich Chemicals, 99.4%) were used without further purification.

The junctions (1×1 mm area) were completed with an evaporated Pb (Wako Chemicals, 99.999%) cross strip (1 mm wide). These operations were done in a class 10000 clean room (Airtech Japan AER-233C).

The tunneling spectrum was obtained by measuring the second derivative of the tunneling current through the junction at liquid-helium temperature (4.2 K). The circuit was of the bridge type developed by Adler and Jackson. The details have been described before.[24,25] A 500 Hz AC modulation signal (2—3 mV_{pp}) and a slowly varying DC voltage were applied to the junction. The aluminium or magnesium electrode was negatively biased with respect to the Pb electrode. The second harmonic signal through a notch filter (NF Electronic Instruments 2BE) and a bandpass filter (NF 3BP) was detected with a lock-in amplifier (NF LI-574A).

The performance of the apparatus and procedures were tested by measuring the tunneling spectrum of benzoic acid on Al_2O_3.[25] The peak positions of the spectrum were corrected by −1 meV (−8 cm^{-1}) owing to the energy gap of the superconducting Pb electrode.[1,29] The resolution was estimated to be 2.5 meV (20 cm^{-1}) by measuring the narrowest peak width in the spectrum. The accuracy of the peak position is estimated to be ±0.5 meV (± 4 cm^{-1}).

Results

Tunneling Spectra of Alumina and Magnesia. The tunneling spectra of the undoped Al-Al_2O_3-Pb and Mg-MgO-Pb junction are shown in Fig. 1. The peak positions and features of the spectra agree well with those previously reported.[1-6,11,25] The peaks at 300 and 930 cm^{-1} of the tunneling spectrum of the alumina junction are assigned to the aluminium phonon and the vibrational mode of the aluminium oxide, respectively. The broad peak at 3610 cm^{-1} is assigned to the stretching mode of the surface OH groups. The broadness and asymmetric tailing toward lower frequencies are typical features of hydrogen-bonding hydroxyl groups. The very weak peak at about 2900 cm^{-1} is due to the CH stretching mode of a hydrocarbon contamination; however, the weakness of this peak indicates that the amount of contamination is negligible.

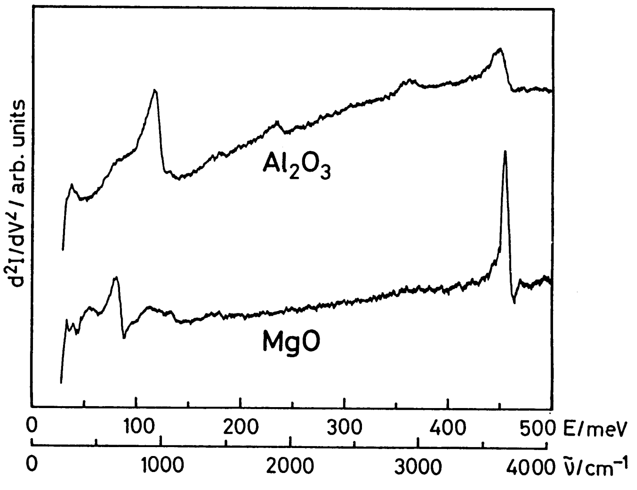


Fig. 1. Tunneling spectra of the undoped Al-Al_2O_3-Pb and Mg-MgO-Pb junction. The oxides were made by an oxygen glow discharge.

The peaks at 430 and 640 cm^{-1} of the tunneling spectrum of the magnesia junction are due to the vibrational modes of MgO. The peak at 260 cm^{-1} arises from the magnesium phonon mode. The strong peak at 3650 cm^{-1} and the shoulder at 3590 cm^{-1} are caused by the stretching vibrations of the surface OH groups. These peaks indicate that there are two types of OH groups on the magnesia surface: An isolated OH and a hydrogen-bonding OH group. These peaks of the spectra of magnesia junctions vary in intensity from sample to sample. There is no peak near 2900 cm^{-1}, and these junctions show no organic contamination. Magnesia junctions doped from water or alcohols gave very noisy tunneling spectra. This instability of the spectrum is probably caused by a change of the surface state of the junction due to the dissolution of the magnesia surface.

Tunneling Spectra of Isomeric Phthalic Acids. The tunneling spectra of phthalic, isophthalic, and terephthalic acid doped onto the alumina and magnesia surfaces from the gas phase are shown in Figs. 2—4, respectively. Their peak assignments are shown in

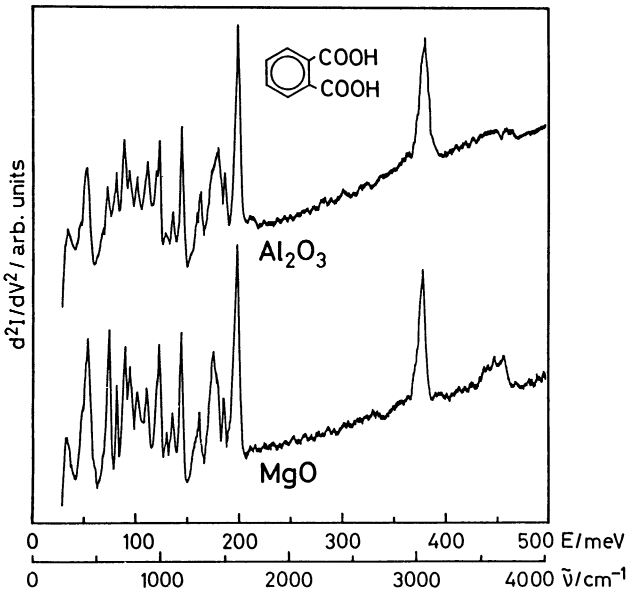


Fig. 2. Tunneling spectra of phthalic acid on Al_2O_3 and MgO doped from the gas phase.

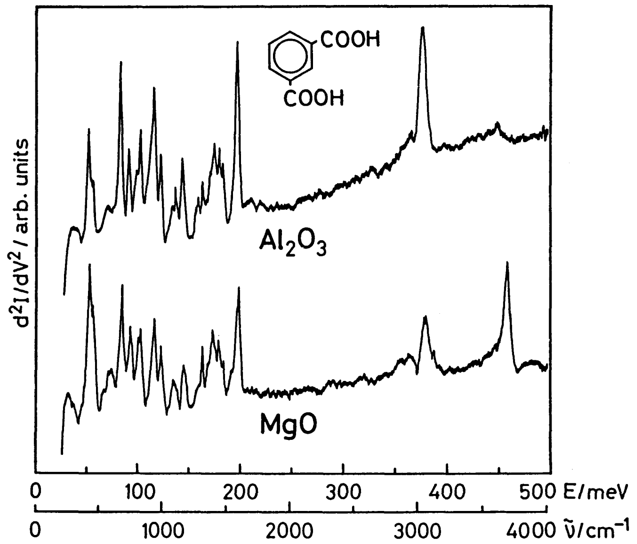


Fig. 3. Tunneling spectra of isophthalic acid on Al_2O_3 and MgO doped from the gas phase.

Table 1. Vibrational Frequencies (cm^{-1}) and Mode Assignments for Phthalic Acid on Al_2O_3 and MgO Doped from Gas Phase Measured by IETS

MgO	Al_2O_3	Al_2O_3 a)	Assignment
3630 m b	3619 w b	3596 w b	νOH (surface)
3038 s	3037 s	3037 s	νCH (20b)
		2894 w b	(contamination)
	1697 vw	1704 vw	νC=O
1588 vs	1585 vs	1588 vs	νCC (8a)
1573 sh			ν_{as}COO$^-$
1484 m	1484 m	1486 m	νCC (19b)
1429 sh			ν_sCOO$^-$
1406 s b	1425 s b	1422 s b	ν_sCOO$^-$
1296 m	1295 m	1296 m	βCH (3)
1264 sh	1268 sh	1260 w	νCX (7a)
1155 s	1151 s	1149 s	βCH (15)
1085 m	1082 m	1081 m	βCH (9b)
1040 m	1036 m	1035 m	βCH (18b)
978 s	980 s	980 s	γCH (5)
957 sh	954 sh	957 sh	γCH (10a)
880 m	886 m	881 m	γCH (10b)
808 m	803 m	802 m	νCC (1)
743 m	743 m	744 m	γCH (11)
708 s	707 m	702 m	γCC (4)
649 m	645 m	644 m	γ_sCOO$^-$
587 s	580 m	582 m	βCC (6b)
548 sh	545 sh		βCC (6a)
422 s	416 s	422 s	β_{as}COO$^-$
382 sh	377 sh	374 sh	?
	295 m	285 w	Al phonon
255 m	267 sh	259 m	βCX (9a)

vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder, b=broad. a) Doped from ethanol solution in Ref. 25.

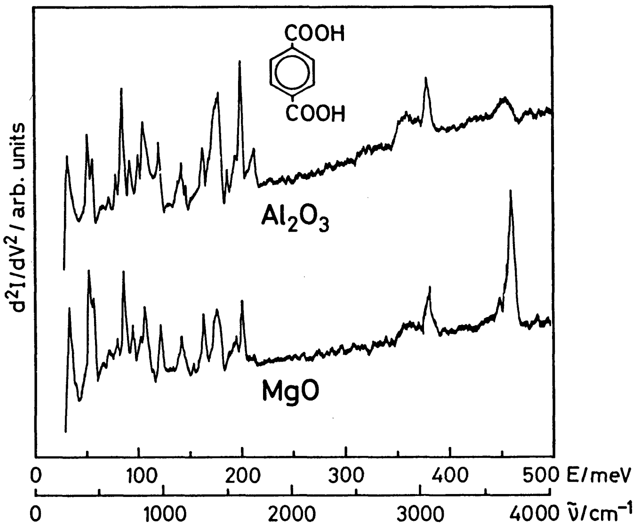


Fig. 4. Tunneling spectra of terephthalic acid on Al_2O_3 and MgO doped from the gas phase.

Table 2. Vibrational Frequencies (cm^{-1}) and Mode Assignments for Isophthalic Acid on Al_2O_3 and MgO Doped from Gas Phase Measured by IETS

MgO	Al_2O_3	Al_2O_3 a)	Assignment
3687 s			νOH (surface)
3616 sh	3617 w b	3621 w b	νOH (surface)
3040 m	3039 s	3038 s	νCH (7a)
2894 w b	2916 w b	2888 w b	(contamination)
	1703 vw	1684 vw	νC=O
1591 s	1586 s	1587 s	νCC (8b)
1544 sh			ν_{as}COO$^-$
1465 vw	1469 w	1467 sh	νCC (19b)
1441 s	1444 s	1441 s	νCC (19a)
1394 s b	1404 s b	1402 s b	ν_sCOO$^-$
1312 m	1309 w	1311 w	νCC (14)
1272 w	1278 w	1281 vw	βCH (3)
1160 m	1156 m	1151 m	βCH (9b)
1095 m	1100 m	1088 w	βCH (18b)
1070 vw	1075 vw	1061 vw	βCH (18a)
989 m	982 m	980 m	γCH (5)
934 m	932 s	930 s	νCX (7b)
827 m	826 m	824 m	νCC (1)
809 sh	799 sh	801 sh	?
744 m	735 m	737 m	β_sCOO$^-$
674 s	670 s	672 s	γCC (4)
597 m b	572 w b	582 w b	βCC (6b)
447 sh	440 sh	440 sh	?
420 s	417 s	418 s	β_{as}COO$^-$
	299 m b	294 m b	Al phonon
251 m			Mg phonon

a) Doped from ethanol solution in Ref. 25.

Tables 1—3. The tunneling spectra of the isomeric phthalic acids doped from alcohol solutions onto the alumina surfaces have been measured, and their detailed assignments and comparison with their infrared and Raman spectra have been shown in our previous paper.25) The peak positions of the spectra doped from ethanol solutions are shown in each table for the sake of comparison. In these tables, stretching, in-plane bending, and out-of-plane bending vibrations are denoted by ν, β, and γ, respectively. The symmetric or asymmetric vibration is indicated by the subscript s or as, respectively. Of the bending

Table 3. Vibrational Frequencies (cm^{-1}) and Mode Assignments for Terephthalic Acid on Al_2O_3 and MgO Doped from Gas Phase Measured by IETS

MgO	Al_2O_3	$Al_2O_3$$^{a)}$	Assignment
3681 vs			νOH (surface)
	3622 m b	3623 m b	νOH
3605 sh			νOH (surface)
3043 m	3041 m	3042 m	νCH (20b, 7b)
2872 w b	2876 w b	2873 w b	(contamination)
	1698 m	1699 m	νC=O
1598 m	1598 s	1594 s	νCC (8b)
1558 m	1556 sh	1550 sh	ν_{as}COO$^-$
1497 sh	1498 w	1493 w	νCC (19a)
1410 s b	1426 s b	1423 s b	βOH, ν_sCOO$^-$
1301 m	1305 m	1302 m	νCX (13)
1136 m	1137 m	1136 m	βCH (9a)
1096 sh	1096 w		?
1006 vw	1006 vw	1003 vw	βCH (18a)
966 m	962 m	963 m	γCH (17a)
		916 vw	γCH (10b)
865 sh	871 sh	867 sh	β_sCOO, β_sCOO$^-$
842 s	842 s	839 s	νCC (1)
818 w	803 w	797 vw	βCH-βCX (18b-15)
731 m	737 m	736 m	βCC (12)
679 s	676 s	677 s	γCC (4)
626 w	627 w	619 w	γ_sCOO, γ_sCOO$^-$
560 w b	556 w b	540 w b	γCC (16b)
437 sh	435 s	436 s	β_{as}COO, β_{as}COO$^-$
409 s	407 s	400 s	γ_{as}COO$^-$ +γCH (5)
	284 sh	298 sh	Al phonon
250 m	254 m	242 m	γCX (5)

a) Doped from ethanol solution in Ref. 25.

modes of the COO$^-$ group, β_s designates the scissoring, β_{as} denotes the rocking and γ_s the wagging mode. The Wilson number for the normal vibration of the benzene ring is shown in parenthesis.

The peak positions of the tunneling spectra doped from the gas phase and ethanol solution agree well with each other within the measurement accuracy. This agreement shows that our apparatus and procedures are suitable for the accurate measurement of tunneling spectra. It also shows that there is no contribution from the solvent to our previous tunneling spectra.

When phthalic acid is adsorbed onto the Al_2O_3 and MgO surfaces, the peak intensities of the surface OH groups decrease, and the weak and broad peaks remain in both spectra. In contrast, the clear and characteristic peaks of the adsorbed phthalic acid appear. The relative intensities of the peaks in both spectra on Al_2O_3 and MgO are similar except for those of βCC(6b) and γCC(4). This similarity suggests the same molecular structure and orientation of the adsorbed phthalic acid on both surfaces. The tunneling spectrum of phthalic acid on MgO has no νC=O peak, while that on Al_2O_3 has a very weak peak at 1697 cm^{-1}. The tunneling spectra on both surfaces have strong and broad ν_s, medium γ_s and strong β_{as} peaks of the COO$^-$ groups. The peak position of the ν_sCOO$^-$ mode on MgO shifts from that of the mode on Al_2O_3 about 20 cm^{-1} toward lower frequencies. The peak of the ν_{as}COO$^-$ mode appears as a shoulder on the very strong peak at 1588 cm^{-1} in the spectrum on MgO. These results show that phthalic acid reacts with the surface OH groups on both surfaces by loosing the protons of the COOH groups and is adsorbed as the benzenedicarboxylate ion onto the surface cations (Lewis-acid sites). The peak shift of the ν_sCOO$^-$ mode may relate to the difference in the interaction between the COO$^-$ groups and the surface cations as suggested by Walmsley et al.[6)]

The tunneling spectra of isophthalic acid on Al_2O_3 and MgO have strong and broad ν_s, medium β_s and strong β_{as} peaks of the COO$^-$ groups. The peak position of the ν_sCOO$^-$ mode on MgO also shifts 10 cm^{-1} toward lower frequencies. The peak of the ν_{as} COO$^-$ mode appears as a shoulder on the strong peak at 1591 cm^{-1} in the spectrum on MgO. The surface OH groups remain on the MgO surface. These results show that isophthalic acid is also adsorbed onto both surfaces as the dicarboxylate ion. The remainder of the surface OH groups on MgO may relate to the orientaion and the surface coverage of the adsorbed isophthalic acid as discussed later.

The tunneling spectrum of terephthalic acid on Al_2O_3 doped from the gas phase has a medium νC=O peak in addition to the νCOO$^-$ peaks. The spectrum is identical with that doped from the ethanol solution,[25)] and it is concluded that terephthalic acid doped from the gas phase is also predominantly adsorbed onto Al_2O_3 as the monocarboxylate ion. On the other hand, the spectrum on MgO has the COO$^-$ peaks with no νC=O peak and it shows that terephthalic acid is adsorbed onto the magnesia surface as the dicarboxylate ion. Because terephthalic acid is adsorbed as the dicarboxylate ion, its benzene ring must be parallel to the surface. The surface OH groups remain as in the case of isophthalic acid. The peak position of the ν_sCOO$^-$ mode on MgO also has a shift of 16 cm^{-1} toward lower frequencies. The features and the relative peak intensities of both spectra on Al_2O_3 and MgO are independent of the doping conditions of the gas pressure: 60—240 mTorr, and the exposure: 10—60 min.

Comparison of Tunneling Spectra of Isomeric Phthalic Acids. The tunneling spectra of the isomeric phthalic acids adsorbed onto Al_2O_3 have previously been measured by Oxley et al.[23)] They concluded that these acids are adsorbed as the dicarboxylate ions onto Al_2O_3. A comparison of their spectra showed that most of the peak positions and the features of their spectra of phthalic and isophthalic acid agreed with those of our spectra. However, their spectrum of terephthalic acid has no νC=O peak, and disagreed with ours. We examined the experimental conditions in detail and found that the peak intensity and the features of the spectrum of terephthalic acid strongly depend on the solvent used. The spectrum of terephthalic acid doped from a solution of methanol, ethanol, or 1-propanol onto Al_2O_3 has the νC=O peak. However, it has a very weak νC=O peak in the case of an aqueous solution. The weakness of the νC=O peak indicates that terephthalic acid is adsorbed onto Al_2O_3 predominantly as the dicarboxylate ion. The spectra of phthalic and isophthalic acid have no such solvent dependence.[25]

The reason of this discrepancy between our spectrum of terephtalic acid and that measured by Oxley et al. is not clear. However, it seemed to us that the amount of the terephthalic acid adsorbed onto the alumina surface was so small that the νC=O peak disappeared in their spectrum. We concluded that the tunneling spectrum of terephthalic acid doped from the gas phase onto Al_2O_3 also has the νC=O peak, and that terephthalic acid is adsorbed predominantly as the monocarboxylate ion as in the case of the alcohol solutions.[25]

Lewis and Field[26] have also reported the tunneling spectra of the isomeric phthalic acids on Al_2O_3 doped from an ethanol solution. They concluded that these acids are adsorbed as the monocarboxylate ions. We compared the peak positions in their tunneling spectra with those in ours and found that all the peak positions in their spectra have shifts of 15—225 cm^{-1} to higher frequencies. This comparison of the peak positions in the tunneling spectra of terephthalic acid on Al_2O_3 is shown in Table 4. Their assignments for the peaks are completely different from ours. For example, they assigned the strong peak at 1638 cm^{-1} to the νC=O peak, which corresponds to the νCC (8b) peak at 1598 cm^{-1} in our spectrum. No assignment was given to the weak peak at 1735 cm^{-1}, which corresponds to the νC=O peak in our assignment. These peak shifts in their tunneling spectra may be caused by parasitic resistances in the tunneling junctions as indicated by Oxley et al.[23] A comparison between the spectra of terephthalic and *p*-acetylbenzoic acid adsorbed onto Al_2O_3 and MgO clearly shows the presence of the νC=O peak in the tunneling spectrum of the adsorbed terephthalic acid on Al_2O_3 and the absence of the νC=O peak in that on MgO as is shown in Fig. 5.

Table 4. Comparison of Vibrational Frequencies (cm^{-1}) for Terephthalic Acid on Al_2O_3 Measured by IETS

This work		Lewis and Field[a)]		Oxley et al.[b)]	
3622	m b			3621	s
3041	m	3266	m	3052	m
		3112	s		
		2966	s		
2876	w b	2928	s	2931	s
1698	m	1735	w		
1598	s	1638	s	1605	s
1556	sh			1582	sh
1498	w			1518	sh
1426	s b	1462	s	1427	s
				1380	sh
1305	m	1349	m	1300	s
		1249	w	1211	m
1137	m			1152	m
1096	w	1146	w	1112	sh
1006	vw	1083	w	1022	sh
962	m	982	m	946	m
871	sh			888	sh
842	s	871	s	835	s
803	w			774	m
737	m	763	w		
676	s	705	m	695	s
627	w			635	m
556	w b				
435	s			472	s
407	s			410	s
287	sh				
254	m				

a) Ref. 26. b) Ref. 23.

Discussion

Surface Structure of Alumina and Magnesia. Knözinger and Ratnasamy[20] have proposed the surface models of the ideal planes of γ- and η-Al_2O_3. Though the oxygen lattice is more densely packed in γ-Al_2O_3 than in η-Al_2O_3, both aluminas have defect spinel lattices and the local ionic configurations of the Al^{3+} cations are identical. The preferentially exposed faces are considered to be the (110)- and (111)-faces of γ- and η-Al_2O_3, respectively. Because the net charge

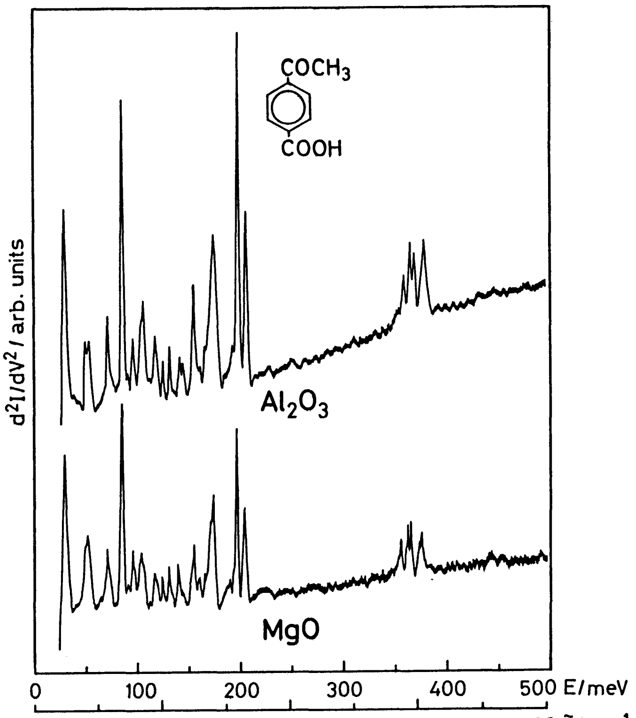


Fig. 5. Tunneling spectra of *p*-acetylbenzoic acid on Al_2O_3 and MgO doped from the gas phase.

in a stable ionic structure should be equal or nearly equal to zero, OH anions are favorable to terminate these faces. From a consideration of the configuration of the aluminium cations and the OH anions, and the coordination numbers of the OH anions, they have shown that there are five types of OH groups on the (111)-face and three types of OH groups on the (110)-face.

The surface OH groups on these faces have different net charge and relate to their different acidity and basicity. The protonic acidity of the OH groups decreases as the net charge on them becomes more negative, while their basicity increases at the same time. The infrared spectra of alumina surfaces have five bands in frequency range 3700—3800 cm^{-1}. They have assigned the band of highest frequency (3800 cm^{-1}) to the most negative OH group with the highest basicity, while the band of lowest frequency (3700 cm^{-1}) is attributed to the most positive OH group with the lowest basicity. The remaining three bands are assigned with decreasing frequency to the corresponding configurations with increasingly positive net charge. Hydrogen bonding between adjacent OH groups perturbs the acidity and basicity, and thus the frequencies of the OH groups to some extent at high OH densities.

The tunneling spectrum of the alumina surface shows the νOH mode in the frequency range 3500—3700 cm^{-1}. The frequency is shifted downward by about 100 cm^{-1}. This shift is due to the image dipole effect of the top lead electrode.1,29) Using several top metal electrodes and an image dipole theory, Kirtley and Hansma29) have shown that the νOH mode of hydroxide ions on Al_2O_3 has a shift of approximately 15 meV (120 cm^{-1}), however, the shifts of the vibrational modes of the adsorbed benzoate ion are less than 0.5 meV (4 cm^{-1}). Judging from the broadness and asymmetric tailing toward lower frequencies, there seems to be more than one type of surface OH group on the alumina surface. These appear to interact with each other through hydrogen bonding. The surface model proposed by Knözinger and Ratnasamy20) is useful to explain the surface structure of the tunneling junction of Al_2O_3.

Magnesia has the structure of NaCl and the external surface of its crystal is predominantly the (100)-face. It has a more ionic character than Al_2O_3 because the electronegativity difference is larger between Mg and O than between Al and O. According to the hydration characteristics and the infrared spectra, Anderson et al.16) proposed a simple model for the chemisorption of H_2O on this face; the (100)-face consists of a collection of an isolated OH group coordinated on a surface magnesium cation and a second set of OH group formed by the remaining protons and adjacent O^{2-} ions. The second type of OH group interacts with their neighbors through hydrogen bonding. A sharp band at 3752 cm^{-1} has been assigned to the νOH mode of the first OH group, whereas a broad band at 3610 cm^{-1} has been attributed to the second group.16)

The tunneling spectrum of MgO also shows a strong and sharp peak at 3650 cm^{-1} and a broad peak at 3590 cm^{-1}, these correspond to the isolated and hydrogen-bonding OH group suggested by Anderson et al.16) The peak positions are shifted downward due to the effect of the top Pb electrode as in the case of the OH groups on Al_2O_3. It is expected that the isolated OH group has higher reactivity and basicity because it is isolated and has the more negative net charge.

Orientation of Adsorbed Isomeric Phthalic Acids. The vibrational spectra of the adsorbed isomeric phthalic acids on metal surfaces have been measured by surface-enhanced Raman spectroscopy (SERS),27) external reflection infrared spectroscopy (RAIR),28) and IETS.25) Moskovits and Suh27) used SERS to investigate the surface geometry of the adsorbed isomeric phthalic acids on colloidal silver particles from aqueous solutions. The SERS spectra of the isomeric phthalic acids had peaks of the COO^- groups but no C=O group and showed that these acids are adsorbed as the dicarboxylate ions onto the surfaces. However, the spectral features of phthalic acid were quite different from those of the others. They attributed this difference to different surface-bonding geometry, and concluded that phthalic acid is adsorbed with its benzene ring perpendicular to the surface, while isophthalic and terephthalic acid are adsorbed parallel to the surface.

Boerio et al.28) investigated the adsorption of terephthalic acid and terephthalic-d_4 acid onto aluminium mirrors from dilute solutions in ethanol by RAIR. The spectra of both terephthalic acids showed a strong and characteristic νC=O band of the undissociating COOH group near 1700 cm^{-1} in addition to the bands of the COO^- groups. Because the ν_s and ν_{as} mode of the COO^- groups were observed, they have concluded that terephthalic acids are adsorbed as the monocarboxylate ions with a vertical conformation in which the benzene rings are perpendicular to the surface but the twofold symmetry axes are inclined at least several degrees from the normal to the surface.

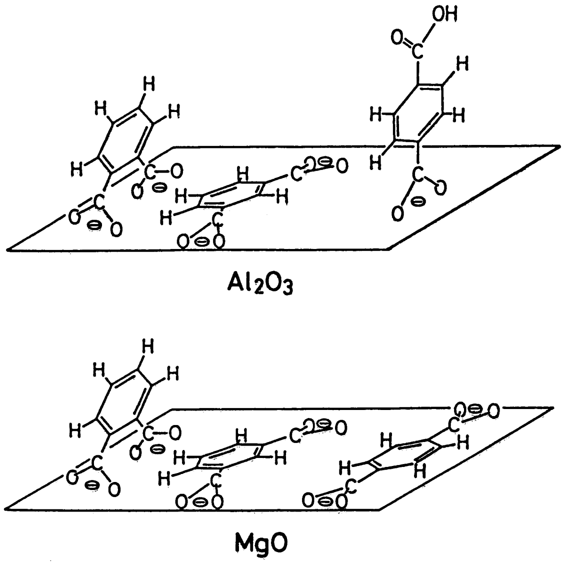
The adsorption and orientation of isomeric phthalic acids on Al_2O_3 from alcohol solutions have been studied in our previous paper using IETS.25) It was found that these acids are adsorbed onto the alumina surface with their own molecular structures and orientations at saturation coverage; phthalic and isophthalic acid are adsorbed as the dicarboxylate ions with their benzene rings almost perpendicular and parallel to the surface, respectively. Terephthalic acid is adsorbed as the monocarboxylate ion almost perpendicular to the surface. Hydrogen bonding through the COOH groups of the adsorbed hydrogen terephthalate ions was observed.

Ogawa et al.[30] have reported the selective monomethyl esterification of dicarboxylic acids adsorbed onto Al_2O_3. Terephthalic and isophthalic acid adsorbed onto Al_2O_3 reacted with diazomethane to give predominantly the monomethyl esters, however, the reaction of phthalic acid was unsuccessful. They have suggested that terephthalic and isophthalic acid are adsorbed onto Al_2O_3 as the monocarboxylate ions, and the unreacting COOH groups are preferentially esterified. The lack of reactivity of phthalic acid was explained by the close proximity of the two COOH groups and the forced orientation of the second COOH group.

Though reactivity is not necessarily a measure of surface orientation of adsorbed species, the orientations and molecular structures of phthalic and terephthalic acid on Al_2O_3 suggested by Ogawa et al.[30] are identical with those observed by IETS. It seems that isophthalic acid which is only weakly bonded to the surface as the monocarboxylate ion may react to give predominantly the monoester. These results indicate that IETS is useful to investigate the surface reactions on an alumina catalyst, and also show that the orientation of the adsorbed species plays an important role to determine the reactivity and selectivity of the surface reaction.

The similarity of the spectral features of the tunneling spectra of phthalic and isophthalic acid adsorbed onto Al_2O_3 and MgO from the gas phase indicates that these acids are adsorbed in the same molecular structure and orientation onto both surfaces. Thus, it can be concluded that phthalic acid is adsorbed as the dicarboxylate ion with its benzene ring perpendicular to the alumina and magnesia surface, while isophthalic acid is adsorbed as the dicarboxylate ion parallel to the alumina and magnesia surface. However, the tunneling spectra of terephthalic acid adsorbed onto Al_2O_3 and MgO show different molecular structure and orientation on both surfaces. It is adsorbed as the monocarboxylate ion onto Al_2O_3; however, it is adsorbed as the dicarboxylate ion onto MgO. A schematic representation of the isomeric phthalic acids adsorbed onto alumina and magnesia surfaces is shown in Fig. 6. Also shown are their dissociation constants in water.

Judging from the dissociation constants of the isomeric phthalic acids, one would expect that phthalic acid is adsorbed predominantly as the monocarboxylate ion because the difference between the two dissociation constants is largest. However the tunneling spectra show that both phthalic and isophthalic acid are adsorbed as the dicarboxylate ions onto Al_2O_3 and MgO. It is clear that the structures and the orientations of these acids on the surfaces are not explained by their dissociation constants. In the case of phthalic and isophthalic acid, when they are adsorbed at one of the COOH groups, the other COOH group seems to be very close to the surface. Thus, the COOH group dissociates more easily than would be expected from their second dissociation constants. According to the molecular models, phthalic acid is adsorbed with its benzene ring almost perpendicular to both surfaces, while isophthalic acid is parallel to the surfaces. The molecular structures and the orientations are identical to those observed on silver colloidal surface by SERS.[27]



	o-	m-	p-
pKa_1	2.95	3.70	3.54
pKa_2	5.41	4.60	4.46

Fig. 6. Schematic representation of the adsorbed isomeric phthalic acids on Al_2O_3 and MgO. Their dissociation constants in water are also shown.

The difference in the molecular structure and orientation of the adsorbed terephthalic acid on Al_2O_3 and MgO seems to be caused by the different structures and reactivity of the surface OH groups on both surfaces. The surface OH groups on Al_2O_3 interact with each other through hydrogen bonding. This hydrogen bonding seems to some extent to prevent the reaction between the COOH groups and the surface OH groups. On the other hand, MgO has the isolated OH group on the surface. The OH groups on MgO are expected to have higher reactivity than the OH groups on Al_2O_3. When terephthalic acid is adsorbed onto MgO, both COOH groups easily dissociate to give the dicarboxylate ion with its benzene ring parallel to the surface because of the high reactivity and basicity of the surface OH groups. The remainder of the OH groups on the magnesia surface may relate to the surface coverage; the coverage of the surface by the adsorbed terephthalate ion may make some surface OH groups inactive because of the hindrance of the benzene ring. On the other hand, it seems that the undissociating COOH group of the adsorbed hydrogen terephthalate ion can not interact with the surface OH groups on Al_2O_3 because of the medium reactivity and the hydrogen bonding of the surface OH groups. Thus, the adsorbed terephthalic acid on Al_2O_3 remains as the monocarboxylate ion with its benzene ring almost perpendicular to the surface at saturation coverage. The hydrogen bonding through the undissociating COOH groups of the adsorbed hydrogen terephthalate ions seems to make them stable on the alumina surface.

Concluding Remarks

IETS is a useful analytical tool for investigating the alumina and magnesia surfaces and the adsorbed species on them. It reveals the different orientations of terephthalic acid adsorbed onto Al_2O_3 and MgO. This difference is caused by the different surface properties of both oxides.

The authors wish to thank Professors Kerry Wayne Hipps and Ursula Mazur of Washington State University for their critical reading of the manuscript and for the valuable comments. The present study was partially supported by a Reseach Aid of the Inoue Foundation for Science No.025.

References

1) P. K. Hansma, "Tunneling Spectroscopy," Plenum, New York (1982).

2) W. M. Bowser and W. H. Weinberg, *Surf. Sci.*, **64**, 377 (1977).

3) S. Gauthier, S. de Cheveigné, J. Klein, and M. Belin, *Phys. Rev. B*, **29**, 1748 (1984).

4) J. G. Adler, *Solid State Commun.*, **7**, 1635 (1969).

5) J. Klein, A. Léger, M. Belin, D. Défourneau, and M. J. L. Sangster, *Phys. Rev. B*, **7**, 2336 (1973).

6) D. G. Walmsley, W. J. Nelson, N. M. D. Brown, and R. B. Floyd, *Appl. Surf. Sci.*, **5**, 107 (1980).

7) N. M. D. Brown, W. J. Nelson, R. J. Turner, and D. G. Walmsley, *J. Chem. Soc., Faraday Trans. 2*, **77**, 337 (1981).

8) D. G. Walmsley, W. J. Nelson, N. M. D. Brown, S. de Cheveigné, S. Gauthier, J. Klein, and A. Léger, *Spectrochim. Acta, Part A*, **37**, 1015 (1981).

9) W. Plesiewicz and J. G. Adler, *Phys. Rev. B*, **34**, 4583 (1986).

10) M. C. Gallagher, Y. B. Ning, and J. G. Adler, *Phys. Rev. B*, **36**, 6651 (1987).

11) S. Kamata, M. Higo, S. Mizutaru, and Y. Owaki, *Rep. Asahi Glass Found. Ind. Technol.*, **49**, 191 (1986).

12) S. Kamata, M. Higo, Y. Owaki, and H. Hayashi, *Rep. Asahi Glass Found. Ind. Technol.*, **51**, 263 (1987).

13) M. Higo, Y. Owaki, and S. Kamata, *Chem. Lett.*, **1987**, 1567.

14) M. Higo, Y. Owaki, and S. Kamata, *Chem. Lett.*, **1987**, 2009.

15) J. B. Peri, *J. Phys. Chem.*, **69**, 211 (1965).

16) P. J. Anderson, R. F. Horlock, and J. F. Oliver, *Trans. Faraday Soc.*, **61**, 2754 (1965).

17) T. Ito, K. Kanehori, and T. Tokuda, *Z. Phys. Chem. N. F.*, **103**, 203 (1976).

18) J. B. Peri, *J. Phys. Chem.*, **69**, 220 (1965).

19) A. A. Tsyganenko and V. N. Filimonov, *J. Mol. Struct.*, **19**, 579 (1973).

20) H. Knözinger and P. Ratnasamy, *Catal. Rev. Sci. Eng.*, **17**, 31 (1978).

21) K. Tanabe, "Solid Acids and Bases," Kodansha, Tokyo (1970).

22) H. Knözinger, *Adv. Catal.*, **25**, 184 (1976).

23) D. P. Oxley, A. J. Bowles, C. C. Horley, A. J. Langley, R. G. Pritchard, and D. L. Tunnicliffe, *Surf. Interface Anal.*, **2**, 31 (1980).

24) S. Kamata and M. Higo, *Chem. Lett.*, **1984**, 2017.

25) M. Higo, S. Mizutaru, and S. Kamata, *Bull. Chem. Soc. Jpn.*, **58**, 2960 (1985).

26) D. M. Lewis and B. O. Field, *Spectrochim. Acta, Part A*, **41**, 477 (1985).

27) M. Moskovits and J. S. Suh, *J. Phys. Chem.*, **88**, 1293 (1984).

28) F. J. Boerio, J. P. Boerio, and R. C. Bozian, *Appl. Surf. Sci.*, **31**, 42 (1988).

29) J. Kirtley and P. K. Hansma, *Phys. Rev. B*, **13**, 2910 (1976).

30) H. Ogawa, T. Chihara, and K. Taya, *J. Am. Chem. Soc.*, **107**, 1365 (1985).