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Reduction of Clay Surface-sorbed Organometallics During Measurement of X-Ray Photoelectron Spectra (XPS)

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Some organometallic compounds, e.g. Ph_3SnCl, react on the surface of the smectite clay, laponite. Other compounds, e.g. $Br_3TeC_6H_4CH{=}NCH_2CH_2N{=}CHC_6H_4TeBr_3$, are sorbed onto the organophilic surface of cetylpyridinium-ion-exchanged Wyoming bentonite. X-ray photoelectron spectroscopy (XPS) is an appropriate technique with which to examine the nature of the surface-sorbed species; however, it is demonstrated that decomposition of the organometallic can occur when the clay surface is exposed over a period of time to energetic X-rays. Thus, care must be taken with the interpretation of data of which some features may be the result of the XPS experiment.

Keywords: Organotin, organotellurium, smectite clay, X-ray, photoelectron spectroscopy

INTRODUCTION

It has been observed recently that the interaction of phenyltin(IV) halides, specifically Ph_3SnCl and Ph_2SnCl_2, with the surface of the synthetic clay laponite leads to rapid hydrolysis of the Sn–Cl bonds followed by cleavage of the Ph–Sn linkage, probably via an electrophilic mechanism involving proton sites on the clay.[1] The resulting products have been described as tin oxide pillared laponites. During these studies X-ray photoelectron spectroscopy (XPS), a surface-sensitive technique, proved valuable in providing supporting evidence for the characterization of the initial stage of the reaction.[1] It was further demonstrated that the pillaring process could be greatly accelerated when carried out in a sealed Teflon container heated in a microwave oven. XPS examination of the microwaved specimens often revealed a new feature characteristic of a metallic phase on the clay surface. Subsequently, this feature was shown to appear randomly in specimens prepared both by microwave techniques and conventionally in bench-mounted shakers.[1]

Currently work is in progress to examine the tendency of various quaternary ammonium exchanged clays—Wyoming bentonite and laponite—to sorb organometallic species. The affinity of the organophilic surface for the organometallic compounds may be expressed quantitatively via measurement of absorption isotherms, but XPS measurements have also been made to examine the surface-sorbed species. In the case of these quaternary ammonium exchanged clays, evidence was also obtained for the presence of low oxidation states for the metal in the organometallic compound added. It is demonstrated briefly in this paper that these observations are caused during measurement of the XPS spectra. The observations are certainly not without precedent since, for example, similar reductions of nickel(II)[2] and copper(II)[3] to metal have been obereved on clay surfaces on exposure to the X-ray flux; however, we are unaware of previous reports of the phenomenon for organometallic compounds sorbed on clay surfaces.

EXPERIMENTAL

Materials

Laponite RD was obtained from Laporte Industries Ltd; the idealized formula is $Na_{0.7}Si_8(Mg_{5.3}Li_{0.7})O_{20}(OH)_4$.[4] Wyoming bentonite CG grade was obtained from Steetley Minerals, the raw material originating from the Wyoming–South Dakota area of the USA. Organometallic compounds were obtained from Aldrich (Ph_3SnCl) or synthesized by literature methods: $[Br_3TeC_6H_4.CH{=}NCH_2CH_2N{=}$

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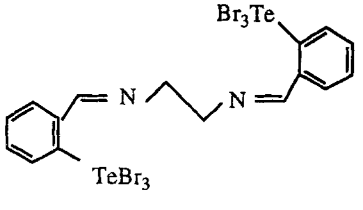
$CHC_6H_4 . TeBr_3$, compound **I**)].[5] Laponite was exchanged with Cu^{2+} ions using the method of Posner and Quirk;[6] similarly Wyoming bentonite was exchanged with cetylpyridinium chloride.



(I)

Organometallic interactions of clay

Four clays were exposed to solutions of organometallic compounds: laponite (Na^+ form), Laponite (Cu^{2+} form), Wyoming bentonite (Na^+ form) and Wyoming bentonite (cetylpyridinium form). Two methods were employed of which illustrations are provided as follows.

Mechanical shaker method

Clay (5 g) was dispersed in ethanol (100 cm^3) and triphenyltin chloride (1.77 g) was added. The mixture was sealed in a flask and placed on a mechanical shaker for seven days. The clay was filtered and air-dried. The product was divided into two portions, of which one was analysed directly by XPS and the second was washed with four 25 cm^3 aliquots of ethanol and air-dried prior to XPS analysis.

Microwave method

Clay (0.5 g), Ph_3SnCl (0.177 g) and ethanol (10 cm^3) were sealed in a Teflon container and subjected to five 1 min bursts of microwave radiation (Sharp Carousel, 700 W) at maximum setting. On cooling, the container was opened and the clay filtered and air-dried. The sample was divided into two parts, of which one was subjected to XPS analysis directly and the other was treated with two 4 cm^3 aliquots of ethanol and air-dried prior to analysis.

Physical methods of analysis

X-ray powder diffraction (XRD)

XRD patterns were recorded with a Philips X-ray diffractometer using Co-K_α radiation. Powders used were preconditioned at 52% relative humidity. The measurements of basal spacings, *d*(001), were used to substantiate the ion exchange of bentonite with the cetylpyridinium chloride. The values obtained from both shaker [17.3 Å (1.73 nm) unwashed, 17.0 Å washed] and microwave oven (17.7 Å for washed and unwashed) are consistent with full exchange.

X-ray photoelectron spectroscopy (XPS)

Spectra were determined with a VG Scientific ESCALAB 200-D instrument using Mg-K_α (1254 eV) radiation. All spectra were internally referenced to the C(1*s*) photoelectron line set to 84.6 eV binding energy. Complex spectra were analysed with a curve synthesis procedure; the analysis was stopped when the simplest fit consistent with a satisfactory reduced χ^2 value was obtained. Measurements were carried out on the pure organometallic compounds to provide data on $\Gamma_{1/2}$ (full width at half maximum) values for the pure components. It is believed that the maximum credible resolution of peaks is ±0.3 eV. One set of experiments involved cetypyridinium-exchanged bentonite which had been exposed to 1,6 - bis(tribromotellurophenyl) - 2,5 - diazahexa - 1,5-diene (compound **I**) as a function of surface irradiation time. These data are displayed graphically in Figs 1 and 2. Other XPS data of relevance to the paper are in Table 1.

The data described in the paper were obtained during the course of investigations with other objectives, by which the selection of some organometallic compounds, such as **I**, was therefore determined.

RESULTS

The XRD data indicate the expected increase in basal spacing for Wyoming bentonite (Na^+ form; *d*(001) = 14 Å) on exchange with large quaternary ammonium species. The values of 17–18 Å are a satisfactory indication of substantial ion exchange. It is noted that the levels of exchange obtained after 5 min in the microwave oven were equally satisfactory to those over seven days on a mechanical shaker. This remarkable acceleration of the ion-exchange process for smectite clays has been noted previously.[7,8]

Exposure of the cetylpyridinium-cation-exchanged bentonites to ethanolic solutions of triphenyltin chloride resulted in the sorption of some of the organometallic compound as indicated by weighing the residue recovered after

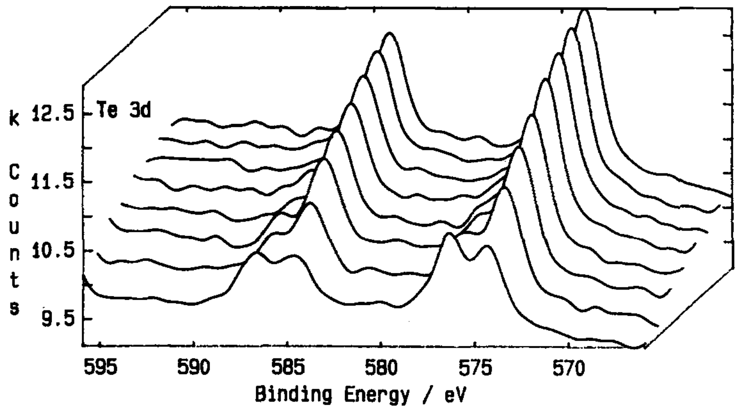


Figure 1 Montage shows 'snapshots' of XPS spectra at intervals over a total period of 220 s X-radiation of the clay surface. Data are for compound **I** sorbed on cetylpyridinium-exchanged Wyoming bentonite. Both Te($3d_{3/2}$) and Te($3d_{5/2}$) peaks are shown.

removal of clay and evaporation of ethanol; the mass balance gave no indication of decomposition of the organometallic. Quantification of the sorption is currently in progress via the measurement of adsorption isotherms. In a similar fashion laponite (Na^+), laponite (Cu^{2+}) and Wyoming bentonite (Na^+) were exposed to ethanolic Ph_3SnCl.

When XPS spectra were determined for clays following exposure to Ph_3SnCl solutions, the presence of tin on the clay surface was clearly indicated by the presence of the Sn($3d_{5/2}$) photoelectron peak. The observed peak was broad, however, with clear evidence of new features at lower binding energy (~483 eV) than the maximum (~487 eV); Fig. 3 is typical. Curve synthesis procedures suggested several tin species to be present (e.g. Fig. 3; Table 1). The two peaks at higher binding energy (487.4, 486.5 eV) are consistent with tin(IV);[9,10] that at 485.1 may suggest tin(II),[9,11,12] whereas the lower energy shoulder (483.2 eV) suggests the presence of tin(0).[9] These observations were general for Ph_3SnCl sorbed on the clays considered here; however, the contribution of the lower-energy components to the total peak intensity was variable and appeared qualitatively to relate to the time of exposure to the X-ray flux. It was likely that the lower-energy components were the result of the XPS experiment. To evaluate this possibility, attention was directed to clay surfaces which had been exposed to tellurium(II) compounds, e.g. $TeBr_4$ or **I**, since the separation of the tellurium(IV) and tellurium(0) photopeaks was more cleanly resolved.[11,12] The XPS spectrum of compound **I** sorbed onto cetylpyridinium-exchanged montmorillonite was measured as a function of time: over 220 s of exposure to X-radiation the spectrum was monitored eight times. Figure 1 shows a montage display of the data in which both the $5d_{3/2}$ and $5d_{5/2}$ regions are visible. Perhaps more instructively, Fig. 2 shows the relative areas of the tellurium (IV) (576.0 eV) and tellurium(0) (573.5 eV) over the period of irradiation. The tellurium(0) peak grows at the expense of the tellurium(IV) peak.

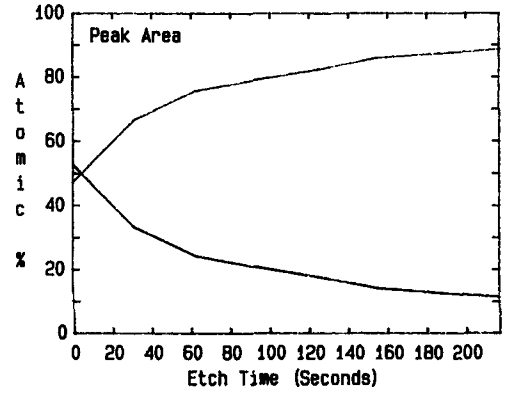


Figure 2 Relative peak areas of the two Te($3d_{5/2}$) components seen in Fig. 1 plotted as a function of time.

DISCUSSION

It has been shown previously[1] that Ph_3SnCl will undergo reactions on the surface of laponite (Na^+). An initial hydrolysis of the Sn–Cl bond is

Table 1 XPS data for organometallic compounds sorbed on clay surfaces

Nature of clay	Organometallic compound	Binding energies (eV) (% area)			
Laponite RD[a] (Na^+)	Ph_3SnCl (shaker, 7 days)	487.6 (27)	486.6 (32)	485.1 (30)	483.3 (11)
	(microwave, 5 min)	487.4 (36)	486.5 (35)	485.1 (20)	483.2 (10)
Laponite RD (Cu^{2+})	Ph_3SnCl (shaker, 7 days)	487.5 (42)	486.6 (39)	485.0(11)	482.9 (7)
	Ph_3SnCl Microwave, 7 min)	487.6 (53)	486.6 (28)	485.0 (14)	483.3 (5)
Wyoming bentonite (Na^+)	Ph_3SnCl (shaker, 7 days)	487.4 (24)	486.6 (32)	485.1 (27)	483.3 (18)
Wyoming bentonite (Q^+)[b] (washed)	Ph_3SnCl (shaker, 7 days)	487.6 (40)	486.6 (38)	485.3 (14)	483.3 (8)
	(microwave, 5 min)	486.9 (79)	486.5 (10)	485.2 (11)	
Wyoming bentonite (Q^+) (exposed to tellurium for 3 days and washed)	$TeBr_4$ (shaker, 10 days)	576.5 (25)	573.6 (25)		
	Compound **I** (shaker, 10 days)	576.0 (13)	573.5 (87)		

[a] Laponite RD (Na^+) is the pure synthetic clay free of additives. [b] Q^+, cetylpyridinium cation.

followed by electrophilic attack at the Sn–C bond (sites of Brønsted acidity) with the ultimate formation of a material described as a tin oxide pillared laponite on the basis of XRD and ^{119}Sn Mössbauer spectroscopic studies. In that work[1] XPS was useful to obtain support for the initial hydrolysis step, in that photopeak binding energies between 486.8 and 487 eV were assigned to molecular species with Sn–Cl bonds and those around 486.6–486.7 eV to species with Sn–O bonds. In the case of some microwaved species, additional peaks at 485.2 eV and 484 eV were seen. However, in subsequent experiments it was shown that the lower-energy peaks could also occur for specimens prepared via the mechanical shaker. The peaks at 485.2 eV [tin(II)] and 484 eV [tin(0)] are attributable to the indicated lower oxidation states of tin.[7]

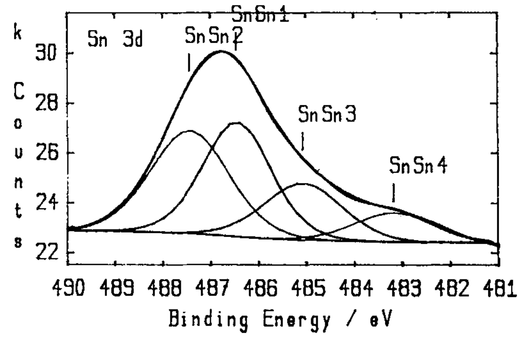


Figure 3 XPS spectrum of Ph_3SnCl sorbed on cetylpyridinium-exchanged Wyoming bentonite, showing curve synthesis analysis.

In this paper the XPS data obtained from a continuation of the laponite work have been combined with data taken from the initial stages of an investigation of the affinity of 'organo'-clays (i.e. clays exchanged with quaternary ammonium type ions) for some organometallic species. In virtually all cases, synthesis of the observed $Sn(3d_{5/2})$ photopeak lineshape suggested the presence of several tin species (a fit to four species gave the best reduced χ^2 values). Since the fitted binding energies of the two higher-energy components differ only by 0.8 eV, it would be unwise to press interpretation byond confirmation of some tin(IV) species being present; what is beyond doubt is the need to include peaks to lower binding energies, consistent with lower oxidation states of tin, to obtain a satisfactory synthesis of the experimental band envelope. It is believed that these peaks arise as a result of exposure of the surface to the X-ray flux during the XPS experiments, and that they do not reflect the particular laboratory histories of the specimens.

A study of perfluoropolyethers by XPS showed decomposition to be initiated by X-ray photons and by secondary electrons created by the photoelectric effect.[13] Given the relatively weak nature of Sn–C (or Te–C) bonds, it is perhaps not surprising that the long exposures to an energetic X-ray flux which may be necessary when the quantity of sorbed organometallic is small should cause decomposition of the sorbed material, even to the metallic state. This point may be more clearly demonstrated by considering the data obtained from clay surfaces onto which tellurium compounds had been sorbed. Two Te($3d_{5/2}$) photoelectron peaks are seen (Fig. 2); that at 576.5 eV ($TeBr_4$/cetylpyridinium-exchanged bentonite) is in excellent agreement with the value reported for $TeBr_4(s)$,[10] whilst the other at 573.6 eV is in reasonable agreement with the value of 573.2 eV reported for Te(0).[14] The data for compound **I** sorbed onto cetylpyridinium-exchanged bentonite are also consistent with the presence of tellurium(IV) and tellurium(0). The observation of this latter spectrum as a function of time of irradiation of the surface by the X-ray flux (Figs 1 and 2) shows that the lower-energy photopeak increases in area at the expense of the higher-energy peak with increased irradiation time.

Since mass balance determination associated with the sorption process shows no discrepancies that could suggest decomposition of the organometallics during the sorption process, and since the pure organometallics give simple XPS spectra from short irradiation times, it is concluded that the prolonged exposure of the organometallic-contaminated clay surfaces to the X-ray flux necessary to obtain signals from the metallic element can cause decomposition ultimately to the metallic state. Thus XPS data for such systems are likely to contain features that originate during the XPS experiment.

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