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The use of XPS spectra for the study of reaction mechanisms: the atom inventory method

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X-ray photoelectron spectroscopy (XPS) allows the analysis of the surface atomic composition of a solid and can be used for mechanistic studies of solid–gas and solid–liquid reactions. The change of atomic composition of a surface after a reaction can be calculated considering hypothetical mechanisms based on the known reactivity of the organic moieties bound to the solid surface. Atom inventory of the elements involved in the reactions was used to quantify the components of the XPS spectrum after the reaction and consequently the change of concentration in at%. The method was used to study the basic hydrolysis and photolysis of the intermediates bound to the carbon matrix after the reduction of SO_2 on activated carbon. Consistent mechanisms were postulated for these reactions. Basic hydrolysis hydrolyzed the sultine intermediate, and the attack of hydroxide ion on the episulfide formed a sulfide anion, eliminating S^{2-} in a consecutive step. Laser photolysis of modified activated carbon in *t*-butanol showed the insertion of the organic moiety in the carbon matrix with expulsion of an SO_2 radical anion that oxidized to SO_4^{2-}. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: solid surface; X-ray photoelectron spectroscopy; intermediates; intermediate reactivity; activated carbon; mechanisms on solids surfaces; basic hydrolysis; photolysis

INTRODUCTION

Physical organic chemistry on solid surfaces and interfaces

Understanding the chemistry on solid surfaces at molecular level is central to many areas of practical interest, especially to new materials. With the development of many surface-sensitive analytical techniques in recent decades, great advances have been made toward understanding this chemistry. Gerhard Ertl was awarded the 2007 Nobel Prize in Chemistry because of his important contribution to the study of structure and reactivity of solid surfaces.

The study of the surface chemistry of relatively complex organic molecules is connected to the selective synthesis of fine chemicals and pharmaceuticals, to applied catalysis, and to the functionalization of materials.[1] When the solid surface decreases, the phenomena become related to nanoparticles and the merging of these systems constitutes another area of great interest.

The general reactivity trends in terms of both the reactants and the nature of the surface can be studied in mechanistic details. The majority of the work of organic chemistry on solid surfaces has been carried out on single-crystal metal or metal oxide surfaces that act as catalysts. The reactions occur through adsorbed species that are not necessarily bound chemically to the surface. Many of the reactions have relevance to industrial catalysis as CO oxidation[2] and hydrogenation,[3,4] ammonia synthesis,[5,6] NO reduction,[7] ethylene hydrogenation,[8] and methanol oxidation.[9]

Surface-science studies of some reactions have allowed postulations to be made about the mechanisms using a variety of techniques such as ultraviolet photoelectron (UPS), high-resolution electron energy loss (HREELS), reflection–absorption infrared (RAIRS), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopies, scanning tunneling microscopy (STM), and temperature-programmed desorption (TPD) techniques.

The studies of the dissociation of saturated C—H bonds have indicated that the reaction may take place either directly upon collision of the incoming gas molecule with the surface or via the

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formation of a weakly adsorbed intermediate trapped on the surface. In the last case, the activation process may proceed via a three-center two-electron intermediate.[10] The reactivity of alkyl halides on early transition metals[11] depends on the activation of the C—X bond and it is sensitive to the structure of the surface and to doping.[12–16]

The loss of hydrogen atoms in hydrocarbon moieties takes place preferentially at the β-position (the second carbon away from the metal site) probably because of the particular stability of the product. Thermal activation of 1,3-diiodopropane produces metallacyclobutane that undergoes β-hydride elimination on Pt(111) to form a stable allyl species.[17]

Silver or ruthenium surfaces covered with oxygen produce surface alkoxides by oxygen insertion into a metal–alkyl bond. Alkoxy intermediates have been postulated from HREELS.[18] Alkyl species couple with the surface alkoxides to form ethers.[19–21] Analogous cross-couplings have been observed between alkyl and alkyl thiolate,[22,23] and between aryl and aryl thiolate[24] on Au.

Cyclotrimerizations of alkynes to aromatics is another typical and well characterized carbon–carbon bond-forming reaction on metal oxide surfaces. As on metals, this reaction appears to involve the initial association of a pair of alkyne units to form a surface intermediate, which then incorporates the third alkyne to yield the aromatic product.[25]

Insertion reactions such as the one described above are quite common in the presence of metal crystals.[26] For instance, the formation of C_3H_6 detected during the thermal conversion of $M{=}CH_2$ moieties on polycrystalline aluminum can be explained by sequential methylene insertion steps.[27]

Adsorbed oxygen can stabilize hydrocarbon intermediates such as alkoxides[28] and carboxylates.[29] It should be noted that the nature of the reactions promoted by the oxygen modification depends both on the nature of the metal surface and on the type of reactant involved. Most of the evidence for oxygen insertion steps on surfaces comes from the detection of gaseous oxygenates, but the direct spectroscopic isolation of alkoxide intermediates has also been achieved in a few instances. For instance, weak HREELS[30] and RAIRS[31] peaks attributable to methoxy species have been observed in the case of the methyl + O/Rh(111) system at low temperatures, and another HREELS study has suggested the presence of both ethoxide and ethyl species in the case of ethyl + O/Ag(110) system.[19,20]

X-ray photoelectron spectroscopy (XPS)

Surface-sensitive analytical techniques allow the analysis of the surface atomic composition of a solid and can be used for mechanistic studies of solid–gas and solid–liquid reactions. XPS is an important technique for surface composition determination. An X-ray beam produces photoelectrons that come from atomic core levels and from the valence band. Photoelectrons that come from the sample surface without energy loss are collected in a spectrum and inform about the binding energy of atomic or molecular levels within energy reach of the incoming X-rays. Small chemical shifts are observed with changes of the oxidation state and electronic environment of each of the components present on the solid surface.[32,33] Final state effects are also important for XPS characterization. These effects inform about how the system is left after photoelectron ejection. Shake-up and shakedown satellites as well as plasmon and other virtual particle creation form relevant part of the XPS spectra. Besides the qualitative information, the XPS technique is used to quantify the atoms at the sample surface. All elements except hydrogen and helium are accessed.

XPS spectra have been extensively used in surface science and the technique has served to postulate mechanisms. For example, the kinetics and energetics of the scission of the C—I bond in adsorbed iodohydrocarbons have been measured using XPS.[34] When 2-iodopropane was adsorbed on O/Ni(100), the XPS results showed the formation of a 2-propoxide intermediate after the oxygeńs insertion into the alkyl–metal bond.[35]

The surface chemistry of Group IV elements

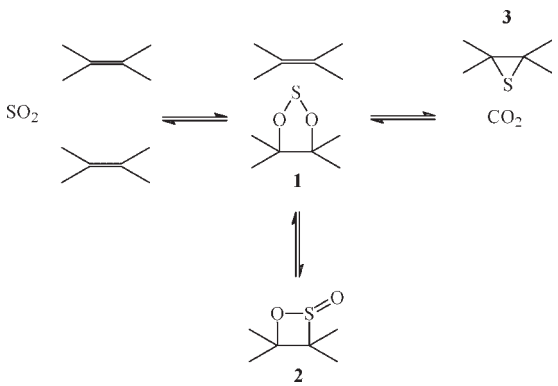
The surface chemistry of Group IV elements has been particularly studied recently because Si, Ge, and C are semiconductors and the surface organic chemistry of these elements may have important use in microelectronics.[36–40] [2+2] Cycloaddition reactions between the π bond of an unsaturated organic molecule such as ethylene and the π bond of the element result in the formation of a four-member ring. Similar mechanisms have been identified upon treatment of the semiconductor surface with organic reactants in solution.[36] Semiconductor surfaces, when treated with HF or NH_4F, lead to the formation of a hydrogen-terminated surface because the non-bonded edges are saturated with hydrides.[41] Double- or triple-bond insertions can be induced on these surfaces using alkenes or alkynes.[42–44]

A great deal of information has been gathered on the reactivity and selectivity of organic molecules on solid surfaces, but this field is still in its infancy. However, within the near future, a better understanding of the surface chemistry of more realistic systems is expected.[1]

The reduction of SO_2 on carbons

Specific studies when are carefully designed to address mechanistic questions can further advance the fundamental understanding of surface reactions using special techniques including kinetic and IR spectroscopy[45] supported by theoretical calculations.[46,47]

Reactions of organic moieties on the surfaces of Group IV elements often involve unsaturated bonds and the organic fragment ends up covalently bound on the surface. The reaction of SO_2 with carbons proceeds through the intermediates 1,3,2-dioxathiolane **1** and 1,2-oxathiene 2-oxide (or sultine) **2**, that decomposes to produce an episulfide **3** and CO_2 (Scheme 1).[48–51] When activated carbon reacts for 3 h



Scheme 1. Mechanism of the primary reaction

with SO_2 at 630 °C, the sulfur concentration increases and the intermediates reach a steady state concentration.[49] The residual carbon is referred to as *modified* carbon.

We have used the change of atomic composition of the surface after a chemical transformation, observed by the XPS spectrum, as information to postulate the mechanisms involved. This method, that we call tentatively the 'atom inventory technique', was outlined in a previous publication on the study of the reactivity of the intermediates bound to the carbon matrix. Consistent mechanisms for several reactions were postulated from the information of the XPS spectra.[52] This technique will be described in detail in this work.

EXPERIMENTAL SECTION

Reagents and methods have been described previously.[52] The activated carbon, from Carbomafra S.A., Santa Catarina, Brazil, was steam activated at 700 °C. It was demineralized in the laboratory by HCl and HF treatment. It had a particle size of 1.68 mm; 0.29% ash content; surface area, 384 m^2/g; and no sulfur was detected.

Solid-state NMR experiments were carried out on an MSL300 (Bruker) with 7.05 T wide-bore magnet and a standard 7 mm double-resonance MAS probe (Bruker). High-resolution solid-state ^{13}C NMR spectra at 75.5 MHz were recorded using cross-polarization (CP). The RIDE pulse sequence was also used for direct detection of ^{13}C with suppression of acoustic ringing effects. Both CP and RIDE spectra were recorded using MAS and high-power ^{1}H decoupling.

Modified activated carbon

The sample of demineralized activated carbon was dried and after cooling it was placed in a tubular stainless steel reactor fitted with a temperature controller and heated by an electric oven in a system that has been described in detail previously.[48] The sample was pretreated at 700 °C for 3 h under a flow of nitrogen controlled at 80 ml/min by a mass flow controller. The temperature was then adjusted to the experimental temperature, and the total gas flow of SO_2 (20% in N_2) was 80 ml/min. The sample was then allowed to react for 3 h since it is known that during this time the intermediates reach the steady state concentration.[49] This residual carbon will be referred as *modified* carbon.

Samples of activated carbon without modification were submitted to the reactions (hydrolysis, photolysis) studied with the modified carbon. The XPS spectra showed changes within the standard deviation of the spectra.

Alkaline hydrolysis

The alkaline hydrolysis of the modified carbon was carried out by refluxing for 24 h a dispersion of a sample in 1 M NaOH aqueous solution. The solid was washed with water and ethanol, and finally dried under vacuum.

Photolysis

A Brilliant B Nd:Yag laser from Quantel was used to irradiate the samples with a discrete number of pulses of known energy (ca. 70 pulses of 15 mJ). The same laser was coupled to a LKS-60 laser flash photolysis system from Applied Photophysics in order to monitor the initial stages of the process. The samples were prepared as suspensions of the modified carbon in quartz cells containing 3 ml of the solvent (*t*-buOH), previously saturated with Ar. All experiments were carried out at the natural pH of the samples and at 25 °C. The solvent was separated by filtration and the solid was washed and dried under vacuum. The solid sample from the photolysis showed a ^{13}C NMR (CPMAS) spectrum with an aliphatic carbon peak at 23 ppm.

Anions, and particularly SO_4^{2-} analysis of the solvent was carried out by electrophoresis, in a Waters system bearing an interchangeable positive–negative power supply, with a UV detector. The detection limit for SO_4^{2-} was ca. 0.1 ppm.

The solvent samples were analyzed by GC/MS performed in a Thermo-Finningan Trace GC 2000/Polaris Q system, using electron ionization. Three different columns were used: J&W, DB-XLB; J&W, DB-5MS; and Supelco SP 2330. No sulfur or organic compounds were detected after exhaustive examination.

The XPS spectra were obtained using a VG Microtech ESCA3000 spectrometer with a 250 mm hemispherical analyzer with nine channeltrons, operating with either an Mg or an Al X-ray source. The X-ray linewidth was of 0.7 and 0.85 eV for Mg and Al sources, which was also the system resolution. The base pressure of the system was in the low 10^{-10} mbar range and the operating pressure was maintained below 10^{-8} mbar during the measurements. The calibration was carried out with respect to the main C1s peak at 284.5 eV. The concentration of the elements was calculated using the system database and is generally known to have a precision of 0.3 at%. The deconvolution of the various peaks was done using the SDP software from XPS International.[53,54] The use of deconvoluted peaks must be made with high experimental sensitivity because this fitting accepts multiple peaks under the same spectral curve.

RESULTS AND DISCUSSION

The atom inventory method

For one step reaction, if $+n_i$ is the number of atoms of the element *i* inserted (or excluded, $-n_i$) from the matrix after the reaction, Σn_i is the total balance of atoms of the elements involved in the reaction and Δ is the extent of the reaction of the element *i* given by Eqn (1):

$$\Delta = \frac{C_i^{\mathrm{i}} - C_i^{\mathrm{f}}}{C_i^{\mathrm{f}}(\Sigma n/100) - n_i} \tag{1}$$

where C_i^{i} and C_i^{f} are the initial and final concentrations of the element *i* in at%.

f is the correction divisor to transform the new surface composition after the reaction in at%:

$$f = \frac{100 + (\Sigma n)\Delta}{100} \tag{2}$$

The final concentration C_i^{f} for each element is obtained from the following equation:

$$C_i^{\mathrm{f}} = \frac{C_i^{\mathrm{i}} + n_i\Delta}{f} \tag{3}$$

where Δ and *f* should be the same for all the elements of the spectrum for that reaction.

Therefore, calculation of Δ and *f* for one element allows the calculation of the final concentration of the rest of elements if the assumed reaction was correct. If the mechanism consists of several steps, the final concentrations calculated for one step are used as initial concentrations for the next step. However, the

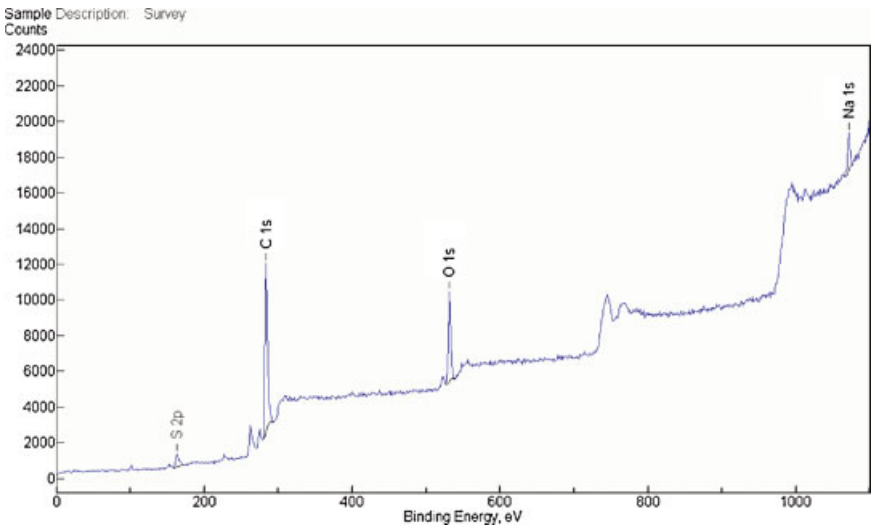


Figure 1. Survey of the XPS spectrum of modified activated carbon after basic hydrolysis at 100 °C [This figure is available in colour online at www.interscience.wiley.com/journal/poc.]

method does not allow distinguishing between reactions with the same stoichiometry.

We will discuss two examples where the atom inventory method was used successfully.[52]

Basic hydrolysis at 100 °C of modified activated carbon

The survey of the XPS spectrum of the product of the alkaline hydrolysis at 100 °C of modified activated carbon is shown in Fig. 1. The elements involved in the reaction are carbon, sulfur, oxygen, and sodium, and the survey provides the surface composition after the reaction in at% for each element. The peaks were deconvoluted and the details are shown in Fig. 2. The comparison of the spectra before and after the reaction can be observed in Table 1. Only the two deconvoluted peaks of sulfur were considered because they can be unambiguously assigned.[54,55] The peak at 164 eV corresponds to non-oxidized sulfur (episulfide) and the peak at 168 eV corresponds to oxidized

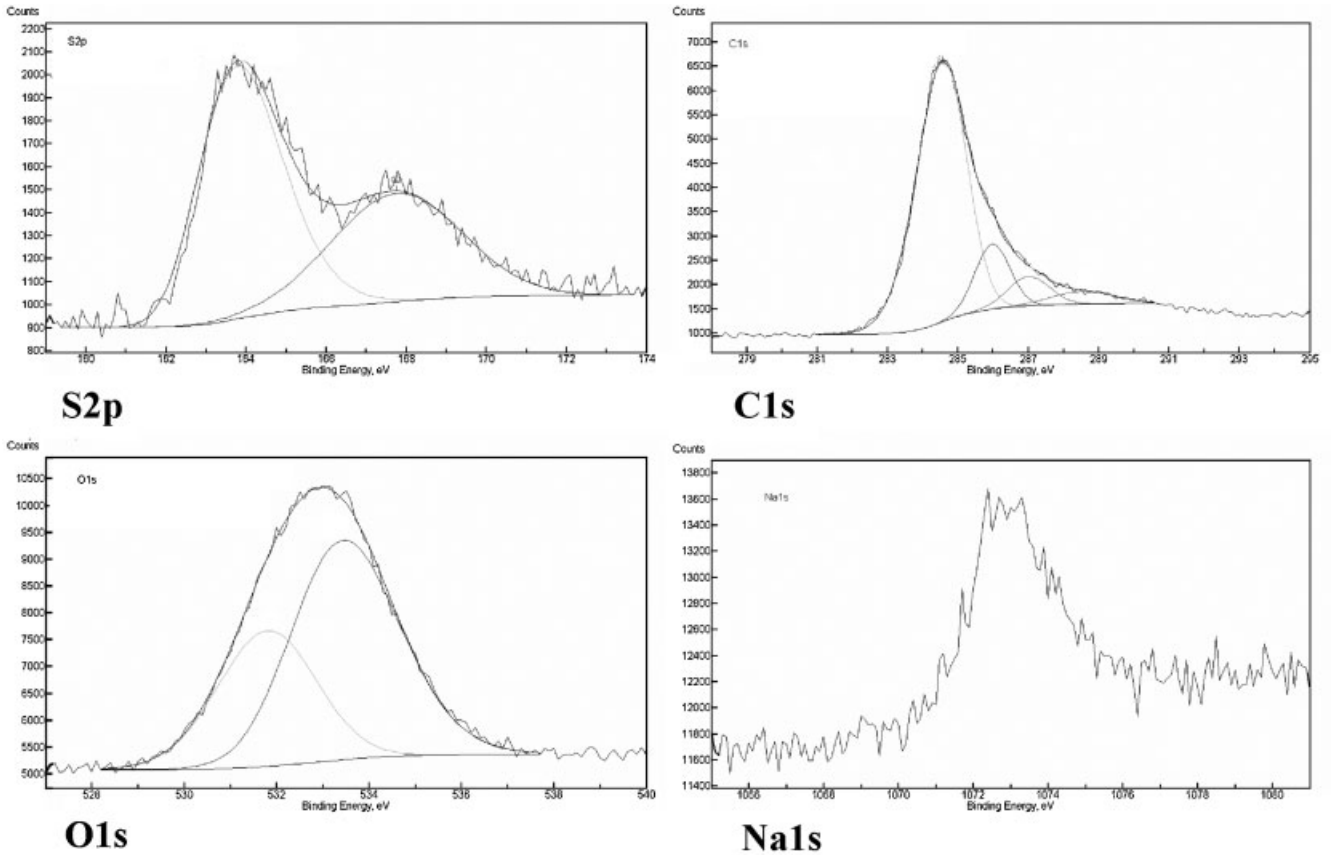


Figure 2. Deconvoluted peaks of the XPS spectrum of modified activated carbon after basic hydrolysis at 100 °C

Table 1. Bond energies and composition from XPS spectrum of modified activated carbon after basic hydrolysis[a]

Sample	Initial		After basic hydrolysis[b]	
Element	eV (weight)	at%	eV (weight)	at%
S2p				
Non-oxi	163.9 (55.2)	3.97	163.8 (60.4)	2.56
Oxi	168.2 (44.8)	3.22	167.8 (39.6)	1.68
Total		7.19		4.24
C1s				
Total	284.5	82.57	284.5	78.51
O1s				
Total	531.8	10.25	531.8	15.40
Na1s			1072	1.85

[a] Spectrum calibrated by reference to C1s (284.5 eV). Weight of the component is in parenthesis.
[b] Refluxed in 1 M NaOH for 24 h.

Table 2. Quantification of XPS spectrum components for the reaction[a] $C(SO_2) \xrightarrow{2NaOH\,H_2O} HO-C()-OH + Na_2SO_3$

Element	n_i	f	Δ	C^i exp	C^f exp	C^f calc
S2p						
Non-oxi	0			3.97	(2.56)	4.03
Oxi	−1	0.984	1.566	3.22	(1.68)	1.68
Total				7.19	(4.24)	5.71
C1s	0			82.57	(78.51)	83.88
O1s	0			10.25	(15.40)	10.41
Na1s	0				(1.85)	0.00
Σn	−1					

[a] C^i and C^f are the initial and final concentration of the element in at%.

sulfur: dioxathiolane in equilibrium with the sultine.[49–51] Table 1 also shows that the reaction decreased the total sulfur content, mainly the oxidized sulfur, and that negative centers neutralized by sodium ions were formed. Because of the restriction mentioned above about the assignment of deconvoluted peaks, we have used only the main peak of carbon and oxygen.

The dioxathiolane intermediate would hydrolyze under basic conditions,[56,57] decreasing the oxidized sulfur with expulsion of SO_2 and formation of sodium sulfite (Eqn (4)).

$$C(SO_2) \xrightarrow{2NaOH\,H_2O} HO-C()-OH + Na_2SO_3 \qquad (4)$$

For this reaction the atom inventory can be worked out as shown in Table 2 where $n_{S\text{-}oxi} = \Sigma n = -1$ because $n_C = n_{Na} = n_O = 0$. The number of oxygen atoms leaving the matrix(SO_2) is counterbalanced by two OHs that are inserted. Calculation of Δ and f over S_{oxi} was done considering Eqns (1) and (2) with the experimental values of C^i and C^f. The calculated values of C^f for $S_{non\text{-}oxi}$, C, and O were obtained from $f = 0.984$ and $\Delta = 1.566$. Of course, for S_{oxi}, C^f calc = 1.68 is equal to the experimental value, but the values for the other elements calculated from Eqn (3) are very different. For the next reaction, these C^f calc values are considered as initial concentrations C^i exp.

The nucleophilic attack of hydroxide ion on the carbon atom of the episulfide ring would form a sulfide anion with Na^+ as the counterion in the first step, [58,59] eliminating S^{2-} in the consecutive step.

$$C(S) + 2NaOH \rightarrow HO-C()-OH + Na_2S \qquad (5)$$

Table 3 shows the calculations for this reaction. Although the C^f calc values are closer to the C^f exp, the value for sodium is still zero, and therefore we have to consider another reaction.

It is also known that basic hydrolysis of sultines can easily occur with nucleophilic attack on the sulfinyl sulfur that would form a sodium salt.[60–66] However, the method does not allow us to distinguish between the formation of sulfinylate (Eqn (6)) and/or the sulfide sodium salt (Eqn (7)) because both reactions

$$C(SO_2) + NaOH \rightarrow HO-C(SO_2^-)Na^+ \qquad (6)$$

$$C(S) + NaOH \rightarrow HO-C(S^-)Na^+ \qquad (7)$$

occur with the same change of number of atoms (Table 4). When calculated with respect to sodium, this final reaction produced an element distribution of the spectrum in excellent agreement with the experimental results. The standard deviation per element was ±0.40. This was the minimum standard deviation obtained out of 15 other possible reactions. A summary of the reactions that produced the final at% composition is found in Table 5, and Scheme 2 shows the mechanisms involved.

Table 3. Quantification of XPS spectrum components for the reaction[a] $C(S) + 2NaOH \rightarrow HO - C() - OH + Na_2S$

Element	n_i	f	Δ	C^i exp	C^f exp	C^f calc
S2p						
Non-oxi	−1	1.014	1.436	4.03	(2.56)	2.56
Oxi	0			1.68	(1.68)	1.66
Total				5.71	(4.24)	4.22
C1s	0			83.88	(78.51)	82.70
O1s	+2			10.41	(15.40)	13.29
Na1s				0.00	(1.85)	0.00
Σn	+1					

[a] C^i and C^f are the initial and final concentration of the element in at%.

Table 4. Quantification of XPS spectrum components for the reactions[a] $C(S) + NaOH \rightarrow HO - C(S^-)Na^+$ $C(SO_2) + NaOH \rightarrow HO - C(SO_2^-)Na^+$

Element	n_i	f	Δ	C^i exp	C^f exp	C^f calc
S2p						
Non-oxi	0			2.56	(2.56)	2.47
Oxi	0			1.66	(1.68)	1.62
Total				4.22	(4.24)	4.09
C1s	0			82.70	(78.51)	79.64
O1s	+1			13.29	(15.40)	14.64
Na1s	+1	1.038	1.921	0.00	(1.85)	1.85
Σn	+2					

[a] C^i and C^f are the initial and final concentration of the element in at%.

Table 5. Bond energies and composition from XPS spectrum of modified activated carbon after basic hydrolysis at 100 °C.[a]

Sample	Initial		After basic hydrolysis[b]		Calc[c]
Element	eV (wt%)	at%	eV (wt%)	at%	at%
S2p					
Non-oxi	163.9 (55.2)	4.0	163.7 (60.4)	2.5	2.5
Oxi	168.2 (44.8)	3.2	167.7 (39.6)	1.7	1.6
Total		7.2		4.2	4.1
C1s					
Total	284.5	82.6	284.5	78.5	79.6
O1s					
Total	531.8	10.3	531.7	15.4	14.6
Na1s			1072	1.9	1.9
				at% SD	±0.40[d]

[a] Spectrum calibrated by reference to C1s (284.5 eV).
[b] Refluxed in 1 M NaOHfor 24 h.
[c] Calculated from the following reactions:
(1) $C(SO_2) \xrightarrow{2NaOH}\xrightarrow{H_2O} HO - C() - OH + Na_2SO_3$ $\Delta S_{oxi} = 1.566$, $f_{S-oxi} = 0.984$.
(2) $C(S) + 2NaOH \rightarrow HO - C() - OH + Na_2S$ $\Delta S_{non-oxi} = 1.437$, $f_{Snon-oxi} = 1.014$.
(3a) $C(S) + NaOH \rightarrow HO - C(S^-)Na^+$ $\Delta_{Na+} = 1.921$ $f_{Na+} = 1.038$.
(3b) $C(SO_2) + NaOH \rightarrow HO - C(SO_2^-)Na^+$.
[d] Standard deviation per element.

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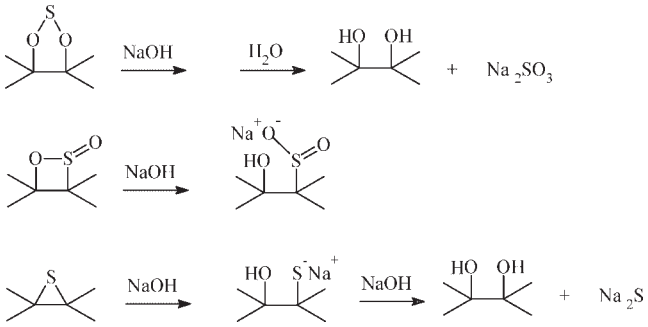


Scheme 2. Mechanism of basic hydrolysis of modified activated carbon at 100 °C

Photolysis of modified activated carbon in t-butanol

Photolysis in *t*-buOH saturated with Ar led to insertion of the *t*-buO group in the carbon matrix, shown as a relatively narrow peak at 23 ppm in the ^{13}C solid-state NMR spectrum. The XPS spectrum components after the irradiation could be quantified assuming the insertion of *t*-buOH with extrusion of SO_2 that was determined as sulfate anion in the solution (Table 6). Calculation of *f* and Δ from S_{oxi} led to the at% of the elements with a standard deviation per element of ±0.28.

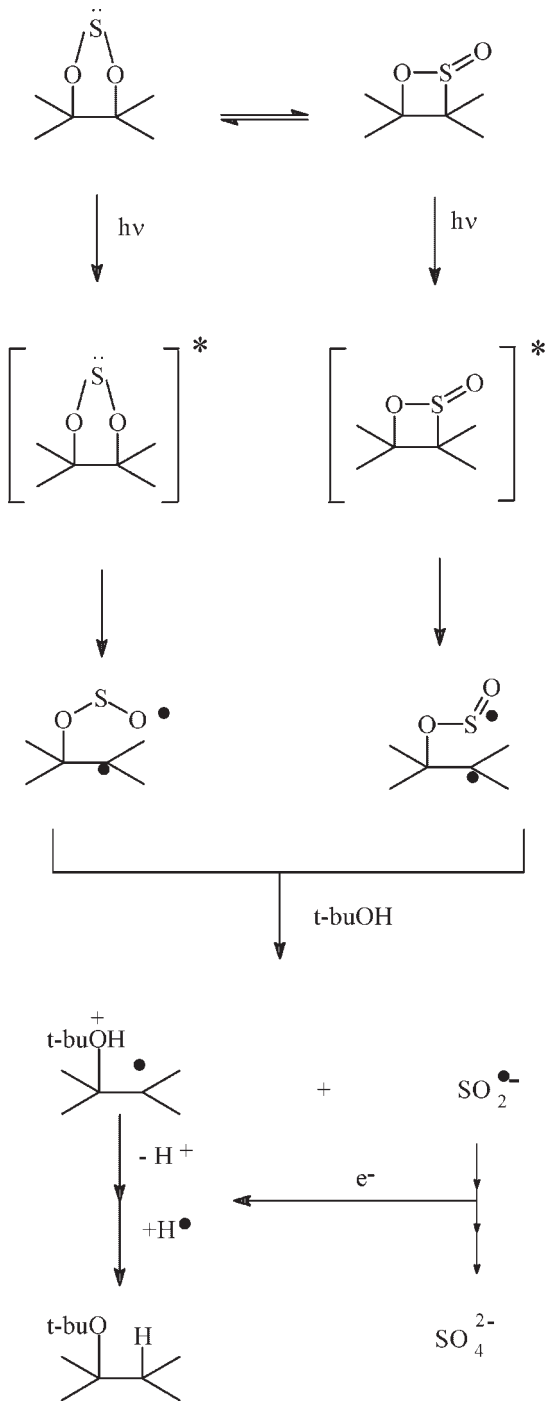
The reaction of insertion of *t*-butoxide and extrusion of SO_2 was also supported by laser flash photolysis experiments.[52] They showed the formation of a broad undefined band between 300 and 500 nm due to $SO_2^{\bullet-}$ whose rate of decay was $3.4 \times 10^6\ s^{-1}$ at 25 °C measured at 300 nm. The oxidation to sulfate occurs after the rate-determining step of the decay. Several pieces of evidence led to the conclusion that the intermediates generated upon light absorption decayed in energy by C—O (dioxathiolane) and/or C—S (sultine) bond homolysis to yield a biradical species. This biradical species reacted with the solvent accompanied by the expulsion of a sulfur dioxide radical anion ($SO_2^{\bullet-}$) and the loss of a proton, yielding the carbon matrix with a *t*-butoxide moiety of the solvent inserted on it and an empty radical position. The so-formed $SO_2^{\bullet-}$ subsequently led to SO_4^{2-} through dimerization and/or mild oxidation.[67] Since the intermediates are in equilibrium, a similar mechanism should occur for both species, the sultine and the dioxathiolane. The proposal in Scheme 3 is the one that best fits the experimental observations. Similar rates of displacement of $SO_2^{\bullet-}$ by *t*-buOH from the sultine and the

Table 6. Quantification of XPS spectrum components for the reaction[a]

$$C(SO_2) + t-buOH \xrightarrow{photolysis} t-buO-C()-H + SO_2$$

				Initial	Final	
Element	n_i	*f*	Δ	C^i	C^f	C^f calc
S2p						
Non-oxi	0			4.1	3.5	4.0
oxi	−1	1.036	1.799	3.0	1.1	1.1
Total				7.1	4.6	5.1
C1s						
Total	+4			81.9	86.0	86.0
O1s						
Total	−1			11.0	9.4	8.8
Σ*n*	+2					
					at% SD[b]	±0.28

[a] C^i and C^f are the initial and final concentration of the element in at%.
[b] Standard deviation per element.



Scheme 3. Mechanism of phototransformation of the oxidized intermediates on modified activated carbon upon irradiation at 266 nm in *t*-butanol

dioxathiolane biradicals are expected, leading to the same radical species shown in Scheme 3.

CONCLUSIONS

XPS is a powerful tool to study the mechanisms of reactions that occur with change of the atomic composition of organic moieties bound to a solid surface.

Atom inventory of the elements involved in the reaction can be used to quantify the components of the XPS spectrum after the reaction and consequently the expected change of concentration in at%.

The changes induced by the reaction to the composition of the solid surface can be characterized further by other analytical techniques such as solid-state ^{13}C NMR, flash photolysis, and GC/MS analysis.

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