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SIMS/XPS Investigations on Activated Carbon Catalyst Supports

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The surface modifications of activated carbon catalyst supports due to HCl treatment were measured in investigations combining X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). The surface properties of carbons derived from beech wood, pine wood, and bitumen were qualitatively characterized by analyzing selected positively and negatively charged fragment ions in SIMS experiments. Surface modification and lot-to-lot variations were found with respect to surface oxygen, aliphatic and aromatic/graphitic carbon, and surface C/H ratios. The surface characteristics of the supports correlated partly with properties of catalytic interest such as the valency and dispersion of precious metals which were deposited on these supports. The interaction between the activated carbon surfaces and precious metal compounds is apparently governed not only by the redox behavior of C/O and heterofunctional groups but also by the concentration of surface hydrogen. The surface hydrogen seems to enhance redox processes in the precious metal impregnation step of catalyst preparation. Therefore, surface hydrogen is an important parameter for controlling catalyst properties in catalyst preparation and should be carefully monitored. © 1994 Academic Press, Inc.

INTRODUCTION

The surface properties of activated carbons used for the preparation of heterogeneous catalysts may vary due to lot-to-lot variations of carbon supports which originate from different natural sources. Therefore, it is essential to monitor and to evaluate the surface characteristics as well as the total porosity, the pore size distribution, and other important parameters.

The effects of oxygen-carrying surface groups together with the microporosity of activated carbon on the adsorption of molecules with different polarity have been studied (1). In addition, a detailed study focused on Pt impregnation of activated carbons with nearly identical pore structure but with profound differences in the specific surface chemistry. This study demonstrated the extent to which the surface effects and the pretreatment of the supports can affect the chemical redox reactions between precious metal atoms and activated carbon (2). Furthermore, it has been shown how changes in the distribution of functional groups containing oxygen on the surface, for example, due to additional acid treatment of carbonaceous supports, can strongly affect the precious metal dispersion of the catalysts prepared on these materials (3).

Both X-ray photoelectron spectrometry (XPS) and secondary ion mass spectrometry (SIMS) are suitable methods which supply detailed information on the surface chemistry of activated carbons which are finely divided and porous. These techniques can be used as additional analytical tools in the quality control of the raw materials and they allow checks to be made of the chemical effects of additional conditioning procedures (4, 5).

By using XPS, it is possible to measure directly the concentration of oxygen and other elements on or near the surface. In addition, it is possible to detect the different classes of surface functional groups in the outermost atomic layers of powdered supports as well as on the outer perimeter of pelletized grades for the production of fixed-bed catalysts (4). The data from XPS can supplement the results obtained from chemical titration techniques on the relative amounts of C/O functional groups (see Refs. (6–8) and literature cited therein).

A specific potential for SIMS measurements in the quality control of carbonaceous catalyst supports is to detect surface contamination, even at very low concentrations. Sputter experiments with increasing material erosion rates or erosion times can distinguish approximately between pure surface impurities and bulk contamination.

According to the natural carbon source and the activation procedures, Na, K, Si, Al, Zn, P, N, Fe, Ca, and other elements can be present on the surfaces of the carbonaceous supports. These can affect certain catalyst applications. Usually an additional acid treatment of the support material is essential to remove, at least partially, the surface contaminants and to reduce the ash content. On the other hand, the acid treatment does not necessarily lead to a stabilization of the catalyst support materials (5). The parameters for these additional treatments have to be worked out, optimized, and controlled in detail.

Furthermore, SIMS, as a mass spectroscopic technique, enables in principle the detection of hydrogen,

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which is bonded in different chemical states. Therefore, SIMS can supplement results on chemically active hydrogen by means of isotope exchange or chemical reactions (Refs. (6–8)) and literature cited therein) or results from classical CHN methods and temperature-programmed desorption (TPD) (9).

A prominent feature in the analysis, especially of pelletized supports, is the high surface specifity achieved under static SIMS conditions, whereas the most suitable technique for studying hydrogen distributions in formed supports from the microscopic up to the macroscopic scale seems to be a further refinement of the elastic recoil detection technique (ERD). ERD, for example, has already been utilized for studying the hydrogen profile in coked alumina catalyst pellets (10).

Experimental results on different carbonaceous materials showed that the SIMS fragment ion signals C_2H^- and CH^- can give a qualitative indication for the hydrogen content in predominantly aromatic/graphitic regions (4, 11–13). Low relative C_2H^- intensities were observed on hydrogen-deficient, graphitized surfaces (11–13). This was in close correlation with measurements on the integral hydrogen content determined by classical CHN methods (12). Enhanced relative CH_x^+ signal intensities, on the other hand, were obtained from predominantly aliphatic surfaces (4, 13).

SIMS experiments on oxidized carbon blacks with enhanced surface concentrations of C/O functional groups have shown that the relative intensities of CH^- or C_2H^- fragment ion signals do not necessarily correspond to enhanced surface concentrations of chemically active hydrogen. Furthermore, these fragments were measured even after eroding the surface regions containing C/O functional groups (14).

The presence of trapped states of hydrogen was concluded from Raman/SIMS work on isotropic and anisotropic graphites (11), employing the CH^- and C_2H^- SIMS signals.

Inelastic incoherent neutron scattering (INS) on coals (bituminous and anthracite) revealed recoiling free protons located inside the material in addition to the well known hydrogen-containing surface groups (15). Coals of different ranks showed different proportions of free and bound protons.

These results and correlations, predominantly measured on aromatic/graphitic materials, were thought to be of possibly practical use in characterizing the surface quality of activated carbon supports for technical applications with respect to hydrogen-related properties. This seems not unlikely with respect to results for Pt supported on carbon blacks (16), showing that for precious metal dispersion and sintering resistance the oxygen surface groups are of similar importance on sp^2 surfaces as reported for sp^2/sp^3 surfaces of activated carbons (3).

In addition to the effects of different surface impurities, indications for a possible correlation have been found between the relative CH^- SIMS signal intensity, which was obtained from pelletized activated carbon supports, and the precious metal dispersion of the final catalysts that were prepared from these materials (4).

Together with the well investigated influence of certain surface groups containing oxygen (see Refs. (3, 7) and the literature cited therein), the amount of hydrogen-containing surface structures, not only of active surface hydrogen from C/O groups, seems to be of additional importance in the catalyst preparation.

In the present study, XPS and SIMS were utilized to determine the effects of HCl treatment on the surface properties of activated carbon supports. The main scope was the attempt to detect changing surface contributions of hydrogen on the prepared surfaces. Observations on different samples of carbon prepared from pine wood, beech wood, and bitumen are compared with data on precious metal/carbon catalysts. The new investigations extend previous work (4, 5).

2. EXPERIMENTAL

2.1. Materials

Different lots of steam-activated pine wood carbon (powdered) and beech-wood carbon (formed, pelletized) supports were analyzed. For comparison, steam-activated bitumen-derived samples (formed) were also measured. The surface areas of all these materials were in the range 1000–1100 $m^2\ g^{-1}$.

For the additional acid treatment, a 2 M HCl solution was used. After HCl treatment the activated carbon was washed with distilled water. Subsequently, the pH of the washing water was adjusted to 2–3 by adding NaOH solution. Finally, the material was washed again with distilled water until a Cl^- test with $AgNO_3/HNO_3$ indicated that chloride had been completely leached out of the carbon. The impurity level on the surfaces of these materials was monitored by means of XPS and SIMS.

For the preparation of the powdered catalysts, the activated carbon was first suspended in distilled water. Then a 25% aqueous solution of hexachloroplatinic acid (H_2PtCl_6) was added. After impregnation and heating to 80°C the suspension was adjusted to pH 10.0 by adding NaOH. After agitation at 80°C, the platinum was reduced by adding formaldehyde. After further agitation the suspension was filtered and washed. A Pt/activated carbon catalyst with 1% Pt (wt%) was obtained.

For the preparation of the fixed-bed catalysts, a 20% aqueous solution of tetrachloropalladous acid (H_2PdCl_4) was added to the activated carbon pellets in a shaker. The volume of the solution containing precious metal was calculated to be 95% of the total adsorption capacity of the activated carbon pellets according to the determined pore volume. After impregnation, the pellets were dried and reduced in a flowing N_2/H_2 (95/5) mixture at 400°C. A Pd/activated carbon catalyst with 1% Pd (wt%) was obtained.

2.2. *XPS and SIMS Measurements*

The XPS/SIMS equipment utilized and the beam parameters were reported in Ref. (4). The base pressure of the spectrometer system was 2×10^{-10} mbar (turbomolecular pumps, ion getter pumps and ending with Ti sublimation pumps and N_2 cryostage) and in the 10^{-9} mbar range during the measurements. All double-stage rotary pumps in the roughing section of the pumping system were equipped with adsorption traps freshly filled with activated aluminum oxide which had been degassed *in vacuo* to prevent any backdiffusion of traces of pump oil into the UHV chambers. The partial pressures of the residual gases, mainly nitrogen, were permanently monitored by mass spectrometers (Quadrex 200, Inficon, multiplier heads). Therefore, any artefacts caused by adventitious hydrocarbons or water picked up in vacuum could be excluded.

Each single sample was introduced using a separate degassing station with a base pressure of 2×10^{-9} mbar. The desorption period of each activated carbon sample was checked by means of mass spectrometry. As soon as stable UHV conditions were established a sample was transferred into the analysis chamber.

The XPS spectra were recorded in the fixed analyzer transmission (FAT) mode (17) at pass energies of 150 eV (survey scans) and 50 eV (detailed scans for binding energy analysis). The binding energy scale was referenced to the Au $4f_{7/2}$ signal at 83.8 eV (18). For spectrometer calibration, the SCAA83 standard materials of the National Physics Laboratory (NPL, Teddington, U.K.) were repeatedly used after sputter cleaning. Uncontrolled variations of the XPS signals caused by a possible partial electrostatic charging of the surfaces especially of formed carbons measured before acid treatment was checked and ruled out by additional experiments using a low energy electron flood gun (Leybold) at varying beam currents or by changing the electrostatic potential of the entrance aperture of the electron analyzer.

For SIMS analysis, Ar^+ ions from a IQ12/38 ion gun (Leybold) with a mass filter were used. A QMG 512 quadrupole mass spectrometer (Balzers) was utilized for the detection of the secondary ions. The ion beam was scanned over the sample surface in an area of 2 mm × 2 mm. The spot size was approx. 200 μm. The quadrupole mass filter was electronically gated to avoid crater edge or periphery effects. Argon was supplied by Messer Griesheim, quality 5.0 (99.999%).

The stability of the ion beam was repeatedly checked by measuring the ion current with a Faraday cup and by probing the stability of the sample current with Picoamperemeters (Keithley 485). The pressure of the argon feedstream of the ion gun was adjusted to a constant pressure by a thermovalve control (Balzers RVG050/UDV135). Control experiments were performed using a low-energy electron flood gun to exclude beam instabilities and artefacts due to uncontrolled surface charging effects. The stability of the beam profile and the long-term stability of the erosion conditions during the measurements were repeatedly monitored by sputter experiments on standard targets (BCR-standard S8F88A, NPL, Teddington, U.K.). Between the measurements a high purity gold target (Demetron, 5N grade, integral contaminations <10 ppm) was repeatedly sputtered at a high erosion rate to exclude memory effects due to a deposition of sputtered material around the entrance aperture of the ion optical system. The following beam parameters were used: 3–5 keV Ar^+, 0.3–3 μA.

2.3. *Data Evaluation*

2.3.1. XPS. For data analysis, a standard DS100-set (Leybold) was used for subtraction of *X*-ray satellites, smoothing by second-order polynomial fit (Shirley type (19)), spline fitted-background subtraction, and peak integration. As relative sensitivity factors, 0.20 was used for carbon and 0.61 for oxygen.

Qualitative lineshape analysis was performed by Gaussian/Lorentzian functions (see Ref. (17), p. 574) according to the Marquardt algorithm (20) (Leybold DS 100 software, version 90 A; Gaussian/Lorentzian ratio 2–3).

The binding energy values reported were referenced to the binding energy scale of the spectrometer, calibrated to the Au $4f_{7/2}$ signal. The signal maxima and peak widths reported were obtained by fitting procedures and were cross-checked to the peak positions of other elements present on the analyzed surfaces (e.g., O, Si, Na, etc.) and to the valence band region.

2.3.2. SIMS. With respect to the matrix-dependence of the secondary ion yields, which were reported in detail only for well-defined surfaces (21–23), only relative changes of the fragment ion ratios were evaluated. The mechanisms of the formation of the secondary ions and cluster ions on high-surface-area technical carbonaceous materials still have to be clarified in detail.

The SIMS parameters adjusted in the present experiments using inert gas ions allow material erosion rates between the regime of pure static SIMS (24) and of depth profiling experiments at higher erosion rates. According to Refs. (22, 24), static SIMS conditions are achieved at a primary ion dose below 10^{13} ions cm^{-2} and only about 1% of the topmost atomic layer is eroded during the analysis.

With 1–3 μA into 2 mm × 2 mm of a carbon surface slightly higher erosion rates are established but the analysis is still confined to the surface regions. A rough estimate shows that up to 5–10 layers may be consumed during the analysis, but a detailed and reliable calculation is not possible. The sensitivity of the surfaces of activated carbons to a controlled ion induced decomposition in a SIMS experiment can vary due to different amounts of functional groups on the surface, due to different degrees of aromatization/graphitization in the surface regions and due to different local structures. For technical activated carbons the surface, selvedge, and bulk structure can still be far apart from the well known turbostratic or lubricostratic order of carbon blacks or especially graphites.

The experiments were not focused on detecting the properties of chemisorbed species (25, 26) or on measuring bulk properties. The C/H fragmentation behaviour of the surface and the selvedge regions of technical catalyst support materials is monitored.

3. RESULTS AND DISCUSSION

3.1. Activated Carbon

3.1.1. Effects of HCl treatment on beech wood activated carbon supports. Figure 1 shows the C/H SIMS fragment ion signals of a steam-activated carbon support derived from beech wood (formed) measured before and after additional HCl treatment.

The absolute intensity of the C/H signals increases due to the removal of surface-oxygen contributions. The C^-/O^- ratio of the corresponding SIMS signals changed from 0.43 to 3.63. Simultaneously, the surface concentration of oxygen, determined by XPS, changed from 18 to 8%. With respect to the results reported for other carbonaceous materials (11–13), the variations of the relative intensities of the C^+/CH_x^+ fragment ions in Fig. 1 indicate that aliphatic surface contributions are partly removed by HCl, too. The corresponding ratio of the negative ions C_2^-/C_2H^- changed from 8.35 to 4.20, which indicates that after removal of the oxygen-enriched and predominantly aliphatic surface layers by HCl, a relatively higher hydrogen concentration is then present on the modified activated carbon surface. This is contrary to observations on pine-wood-derived supports (powdered) (4).

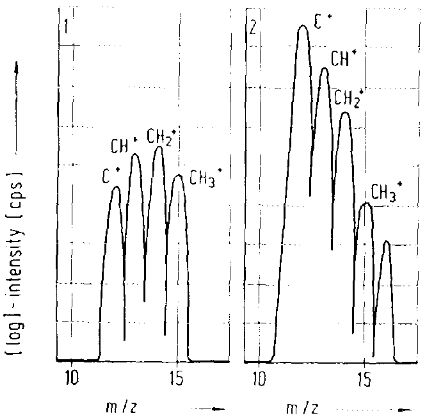

FIG. 1. Changes of the C^+/CH_x^+ fragment ion intensities due to HCl treatment of a beech-wood activted carbon support; logarithmic scale. SIMS parameters: 3 keV Ar^+, 1 μA, 2 mm × 2 mm. (1) raw, steam-activated; (2) after treatment with HCl.

The C^+/CH_x^+ SIMS ion ratios measured on three different lots of a beech wood carbon support after HCl treatment under identical conditions are compared in Table 1. The relative intensity variations of the C/H fragment ion signals are compared with the corresponding XPS data obtained on these samples. The position of the maximum of the C 1*s* signals ranges between 284.5 and 285.1 eV. For aliphatic carbon, binding energy values between 284.6 and 285.3 eV were reported (18, 27), whereas aromatic/graphitic carbon appears around 284.4 eV (27–30).

The simultaneous changes of the XPS signal maxima and the SIMS C/H signal intensities (Table 1) indicate that different relative amounts of sp^2- and sp^3-like states of carbon and of C–OH groups are present. This demonstrates that different surface properties were obtained in these extreme cases in spite of the well-defined conditions of the HCl treatment.

3.1.2. Comparison between beech wood and bitumen-derived activated carbon supports. Figures 2A and 2B show the changes of the relative intensities of negative SIMS fragment ion signals, measured on a bitumen-derived support before and after HCl treatment. The result on carbon from a beech wood support after HCl treatment is also shown in Fig. 2C. The corresponding XPS data are given in Table 2. The enhanced signal intensity of the $C_2H_2^-$ fragment ion in the SIMS spectrum of the bitumen-derived activated carbon ("activate") treated

TABLE 1

XPS and SIMS Results on Three Different Lots of Beech-Wood-Derived Activated Carbon after Treatment with HCl

	XPS		SIMS	
Lot	C 1*s* signal maximum (eV)	Surface oxygen (%)	C^+/CH^+ fragment ion ratio	C^+/CH_2^+ fragment ion ratio
A	285.1	12	0.96	1.68
B	284.7	15	1.31	2.66
C	284.5	9	2.35	5.45

Note. XPS: (%), i.e., percent of area. SIMS parameters: 3 keV Ar^+, 1 μA, 2 mm × 2 mm.

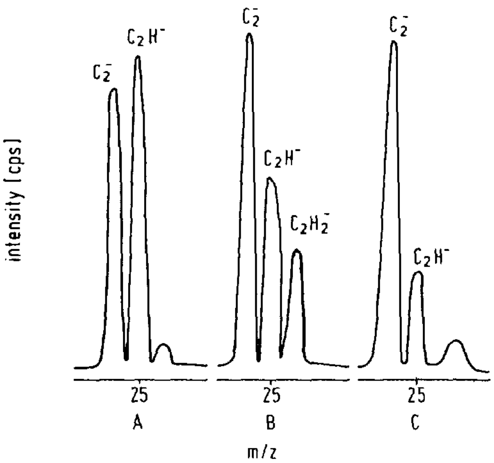

FIG. 2. Fragment ion intensities (negatively charged secondary ions) measured with 5 keV Ar^{+}'3 μA, 2 mm × 2 mm; linear scale. (A) Activated carbon support derived from bitumen, as received; (B) activated carbon support derived from bitumen, after HCl treatment; (C) activated carbon support derived from beech wood, after HCl treatment.

with HCl (Fig. 2B) and the low binding energy position of the C 1*s* signal (284.3 eV, Table 2) indicate that a predominantly aromatic/graphitic surface has been obtained (13). The $C_2H_2^-$ fragment ion is comparatively weak for the still predominantly aliphatic surface of the beech wood carbon sample after HCl treatment (Fig. 2C).

3.1.3. Effects of HCl treatment on pine wood and bitumen activated supports. Table 3 compares the XPS and SIMS data measured on different pine wood carbon supports before and after HCl treatment together with the results on a bitumen-derived activate, similar to that which was characterized in Figs. 2A and 2B. Similarly as observed for the beech wood samples (Table 1), there seems to be a rough correlation between the binding energy position of the XPS C1*s* signal and the relative intensity of the CH_2^+ SIMS fragment ion. The changes of the maxima and of the halfwidths (FWHM) of the C 1*s* signals are due to a superposition of different signal contributions of aliphatic and aromatic carbon as well as of different C–O functional groups in the topmost atomic layers of the samples investigated. These contribute to the whole C 1*s* main signal measured. They are qualitatively related to the oxygen concentration as determined by XPS.

TABLE 2

XPS Results on a Predominantly Aliphatic (Beech Tree) Carbon and an Aromatic/Graphitic (Bitumen) Carbon Support before and after Treatment with HCl (See Fig. 2)

Activated carbon source/pretreatment	C 1*s* signal maximum (eV)	Surface oxygen (%)
Bitumen/as received	284.5	9
Bitumen/HCl	284.3	3
Beech tree/as received	285.0	17
Beech tree/HCl	284.6	8

Assuming that the C_2^-/C_2H^- ratios, reported in Table 3, are a rough measure for the hydrogen content present on these surfaces, additional differences can be derived. The relative intensity of the C_2H^- signal increases due to HCl treatment, which is similar to that for the beech wood carbon activate discussed in Section 3.1.1. This was not the case for the predominantly graphitic/aromatic bitumen activate (Table 3) or for other grades of pine-wood-derived carbon investigated in Ref. (4), which again demonstrates lot-to-lot variations of the support material.

The differences may be due to different degrees of aromatization/graphitization of the activated carbons in the surface regions. Graphitization leads to a decrease of the total hydrogen content and to a simultaneous decrease of the relative intensity of the C_2H^- signal (14).

3.2. Precious Metal Catalysts

3.2.1. Influence of surface properties of activated carbon supports on the precious metal valency of Pt catalysts. Figure 3 compares the carbon 1*s* XPS signals measured on four rather different lots of activated carbon

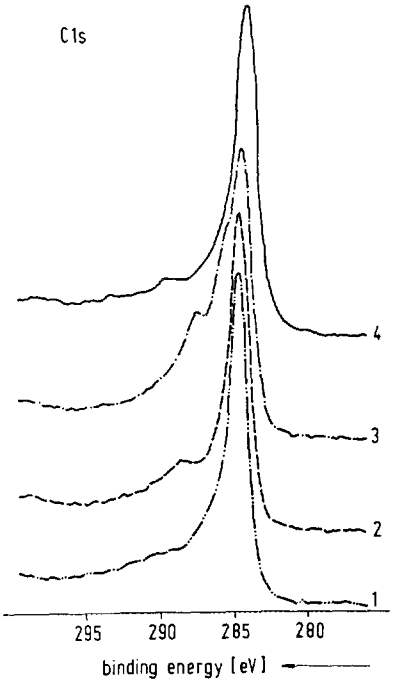

FIG. 3. XPS results. C 1*s* signals of different lots of HCl-treated activated pine-wood carbon.

TABLE 3

XPS and SIMS Results on Different Activated Carbon Supports before and after Treatment with HCl

Carbon source (activated carbon, lot No.)	XPS			SIMS[a]	
	FWHM[b] (eV)	C 1*s* signal maximum (eV)	Surface oxygen (%)	C^+/CH_2^+	C_2/C_2H
Bitumen, HCl	1.0	284.3	3	11.2	1.7
Bitumen, raw	1.2	284.6	8	5.2	0.9
1 pine w, raw	1.4	284.6	7	8.4	1.2
2 pine w, HCl	1.6	284.6	10	3.8	3.7
3 pine w, HCl	1.8	284.6	16	1.7	0.8
1 pine w, raw	1.8	284.7	13	1.3	6.5
4 pine w, HCl	2.0	284.9	16	1.2	3.5
2 pine w, raw	2.4	284.9	20	0.9	4.8
4 pine w, raw	2.7	285.2	26	0.2	4.3
3 pine w, raw	2.9	285.4	38	0.6	9.1

Note. Pine wood (lot nos. 1–4) and bitumen-derived supports (sorted according to increasing peak width of the XPS C 1s signal measured).

[a] Measured with 3 keV Ar^+, 1μA, 2 mm × 2 mm.

[b] Full width at half maximum of the C 1*s* signals measured.

(derived from pine wood, HCl-treated, before precious metal impregnation). The high binding energy features of the signals are due to the presence of different classes of C/O surface functional groups.

In Fig. 4, the Pt $4f_{7/2,5/2}$ XPS signals of two catalysts which were prepared on the supports 1 and 3 are compared (Fig. 3). The shapes of the Pt signals indicate that on the surface of support 3 predominantly reduced Pt has been obtained, whereas on support 1 significant amounts of unreduced Pt species are still present. In Table 4, XPS and SIMS data on the activated carbon supports are compared and the results of XPS band deconvolution by Gaussian/Lorentzian lineshape analyses for estimating the contribution of Pt(0) to the XPS signals measured are given. The peak shape parameters of the Pt $4f_{7/2}$ signal, experimentally determined from the Pt peak of support 3,

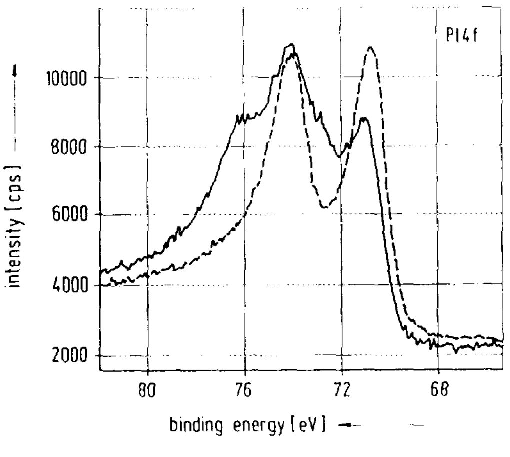

FIG. 4. XPS results. Comparision of the Pt $4f_{7/2,5/2}$ signals measured on the surfaces of two catalysts prepared on different lots of a pine-wood-derived support. *M*; peak maximum of the Pt $4f_{7/2}$ signal, low binding energy edge; Pt(0), 70.9 eV. Straight line: Pt measured on support 1 (Fig. 3); *M* = 71.1 eV. Dashed line: Pt measured on support 3 (Fig. 3); *M* = 70.8 eV.

TABLE 4

XPS and SIMS Results on Activated Carbon (Derived from Pine Wood, Powdered, Treated with HCl) and on the Corresponding Pt/C Catalyst Samples Prepared on These Supports

	Lot no.			
	1	2	3	4
XPS C 1*s*[a] signal maximum (eV)[a]	284.9	284.8	284.6	284.5
Higher energy features (eV)[b]	[c]	287.7[d]	285.9[e] 287.4	289.3[f]
% of Pt(0)[g]	68	74	90	82
SIMS ratios[h]				
C_2^-/C_2H^-	12.1	9.8	3.2	8.4
C^+/CH_2^+	0.3	1.1	2.4	2.3

[a] Reference: Au $4f_{7/2}$ 83.8 eV.

[b] Binding energy values of additional higher binding energy features of the C 1*s* signals.

[c] Predominantly aliphatic surface.

[d] C=O/O–C=O groups.

[e] C–O/C=O groups.

[f] O–C=O/carboxyl groups.

[g] Percentage of reduced Pt estimated by numerical lineshape analysis of the Pt 4*f* region

[h] Measured with 3 keV Ar^+, 0.3 μA, 2 mm × 2 mm.

TABLE 5

SIMS Fragment Ion Ratios Measured on Six Different Lots of HCl-Treated Beech Wood Activated Carbons

Lot no.	ml CO g^{-1}	C_2^-/C_2H^-	C^+/CH_2^+	Enhanced surface concentrations[a]
1	1.21	2.75	3.58	—
2	1.01	3.41	3.11	Ti, Na
3	0.89	3.27	3.02	K, Na, Ca, Fe
4	0.59	3.68	3.31	Si, Ti, Al, Fe, Cl
5	0.57[b]	6.19	1.86	Fe, Ca,[c] Cr, Ni, Br, Si, Al
6	0.39	9.22	0.21	Fe, Ca,[c] Al, Mg, Si

Note. CO sorption values measured on the final Pd catalysts prepared on these supports (sorted according to decreasing CO sorption values).

[a] Determined by SIMS, relative intensities compared to lot no. 1.

[b] Value reported in (4).

[c] Surface carbides, determined by XPS (4).

were used in the curve-fitting procedure. The amount of reduced Pt on the catalyst surface obtained on support 3 is higher than that for the catalyst obtained by impregnating the predominantly aliphatic surface of support 1. In the original state support 3 shows significant concentrations of C–O and C=O groups, lower CH_2^+ but higher C_2H^- SIMS intensities (Table 4).

3.2.2. Influence of surface hydrogen on the precious metal dispersion of Pd catalysts. Table 5 shows the SIMS fragment ion signal ratios C_2^-/C_2H^- and C^+/CH_2^+ measured on a selection of six different lots of HCl-treated beech wood carbon activates before precious metal impregnation. The corresponding Pd/C catalysts obtained on these supports were characterized with respect to the precious metal dispersion measured by CO chemisorption. Furthermore, enhanced surface concentrations of impurities measured on these samples by means of XPS and especially SIMS are noted. Again, these SIMS results qualitatively suggest an additional influence of the amount of surface hydrogen in the precious metal impregnation additional to other important parameters, e.g., the measured surface impurities. With an increasing surface contribution of aliphatic carbon, roughly represented by the CH_2^+ signal and a decreasing amount of surface hydrogen species, represented by the C_2H^- signal, a decrease of the precious metal dispersion on the final catalyst is observed.

4. CONCLUSIONS

Combining XPS and SIMS data allows the monitoring of the effects of standard acid treatment on the surface properties of activated carbon.

As to be expected according to Refs. (2, 3–5), the influence of conditioning procedures such as acid treatment on the amount of surface functional groups containing oxygen and of aliphatic surface contributions can show lot-to-lot variations, but furthermore the partial removal or the modification of surface layers can lead to a surface condition with enhanced relative concentrations of bonded hydrogen on the activated carbon surfaces.

A comparison of selected C/H SIMS fragment ion ratios can be helpful as a rough qualitative measure for this hydrogen content.

As in previous work (4), a correlation between the relative intensities of the CH_x^+ SIMS fragment ions and the positions and widths of the C 1*s* XPS signal has been observed.

The amount of hydrogen, expressed by a higher relative signal intensity of the SIMS fragment ion C_2H^-, together with oxygen-containing surface groups, can be of positive influence on the redox processes of the precious metal impregnation. The precious metal valency as well as the dispersion can be affected.

In addition, to other numerous important properties of carbonaceous catalyst support materials (e.g., surface area, porosity, ash content, micromechanical properties, and distinct classes of C/O C/N, and C/S functional surface groups, or the impurity level in the topmost atomic layers) and in addition to the ASA concept, based on the active surface area and the structural surface heterogeneity (31), the relative amount of hydrogen species seems to be one other important parameter in the catalyst preparation and therefore has to be monitored by adequate methods. Combining XPS data with SIMS results on CH_x^+ and C_2H^- fragments can give a good characterisation of the surface and near-surface region of activated carbon.

A better identification of hydrogen-related properties of activated and modified carbons relevant in the catalyst preparation and a final test of the interpretation of the present SIMS data may be obtained by directly studying the complete proton dynamics of carbonaceous supports by means of the inelastic neutron scattering (INS) technique (15).

With respect to SIMS (14) and X-ray diffraction data on carbon blacks and highly ordered pyrolithic and lower crystalline graphites we suspect that enhanced relative intensities of the CH^- signal roughly represents the fragmentation of predominantly disordered, microcrystalline or amorphous structures containing hydrogen whereas the C_2H^- signal seems to reflect material of higher degree of structural order. In the future comparing STM data on the specific microstructure at the surface of activated carbons (32) and the corresponding results on the SIMS fragmentation characteristics may be helpful to study the impact of chemical and micromorphological properties of the support at an atomic scale on the precious metal impregnation.

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