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Analysis of chemical structure of wood charcoal by X-ray photoelectron spectroscopy*

Received: April 22, 1997 / Accepted: August 18, 1997

Abstract Wood charcoal carbonized at various temperatures was analyzed by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffractometry to investigate the changes of chemical structures during the carbonization process. From the infrared spectra, the carbon double bonds and aromatic rings were seen to form at a carbonization temperature of about 600°C. From the XPS spectra, the ratio of aromatic carbons increased in the temperature range 800–1000°C and over 1800°C. The condensation of aromatic rings proceeded as carbonization progressed. The drastic reduction of electrical resistivity of charcoals was observed in almost the same temperature range. It was found that the condensation of aromatic rings had some relation to the decline in electrical resistivity. Wood charcoal carbonized at 1800°C was partly graphitized, a finding supported by the results of X-ray diffraction and XPS. The functional groups containing oxygen diminished with the increase in carbonization temperature.

Key words Wood charcoal · Chemical structure · X-ray photoelectron spectroscopy · X-ray · Carbonization

Introduction

Much attention has been paid recently to the use of wood charcoal as a source of carbon materials. It has excellent characteristics; moreover, it can be replaced, as we can uti-

lize sustainable forest resources. Highly fire-endurant or electromagnetically shielding materials^{1–4} were developed from wood charcoal with novel performances equivalent to those of metallic materials. They can be used as adsorbents for environmental purification and as materials regulating humidity.^{5–7}

The carbonization process of wood has been the focus for the development of new carbon materials. Wood undergoes several stages of conversion during the carbonization process,⁸ and the chemical structures and properties of wood charcoal are assumed to change depending on the carbonization temperature. The characteristics of wood charcoal are essentially related to the chemical structures formed during the heating process.

Until now, little knowledge has been obtained about the relation between the chemical structure of charcoal and the carbonization temperature. For example, the electrical resistivity of charcoal varies from the insulator to the conductor regions depending on the carbonization temperatures^{4,9}; as a result, the charcoal develops an electromagnetic shielding property. The electrical conductivity of charcoal is believed to originate from its chemical structure, which is still unknown. The changes in the chemical structure of wood charcoal were shown to have some effect on its adsorption properties, which are influenced by the carbonization temperature. To design new wood carbon composites with high and multiple functions, it is necessary to clarify the changes in the chemical structure of wood charcoal during the carbonization process.

In this study, X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffractometry were used to analyze the chemical structure of wood charcoal. XPS, which demonstrates the energy distribution of photoelectrons ejected from the inner shell of the atom by soft X-rays, was mainly used to investigate the state of the chemical bonding in wood charcoal. Because of the darker color and the higher electrical conductivity of charcoal, FTIR and solid-state nuclear magnetic resonance (NMR) were unsuitable for analyzing these materials.¹⁰ From this point of view, XPS is suitable for investigating the chemical structure of wood charcoal.

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*This paper was presented at the 45th Annual Meeting of the Japan Wood Research Society in Tokyo, April 1995 and at the 47th Annual Meeting of the Japan Wood Research Society in Kochi, April 1997

Materials and methods

Sugi (*Cryptomeria japonica* D. Don) logs about 25 years old were obtained from Kochi Prefecture and milled into powder (20 mesh pass). Commercial cellulose powder (No. MN-100; Nacalai Tesque, Japan) was used as a control. The wood meal and cellulose powder were oven-dried at 105°C for 24 h before testing.

Carbonization

For carbonization temperatures below 1400°C, the wood meal and cellulose powder were placed in a heat-resistant box that was covered with layers coke and heated in an electric oven, increasing the temperature 4°C/min up to the desired temperature in an inert atmosphere under normal pressure. After the target temperature was attained, it was maintained for 3 h; it was then allowed to cool naturally, and the charcoal was removed from the oven.

For carbonization temperatures above 1500°C, the samples were precarbonized at 700°C in a nitrogen gas atmosphere to remove the volatile substances and tar included in the raw materials. The precarbonized charcoal was placed in a carbon crucible and then in an ultra-high temperature electric oven (SHC-3000H; ShinMaywa, Japan) and carbonized in an argon gas atmosphere. The specimens were heated at a rate of 10°C/min and maintained for 1 h at the target temperature. Finally, the furnace was cooled to 600°C at the same rate as the heating process to protect the carbon electrode and then cooled naturally.

Charcoal characterization

The FTIR, XPS, and X-ray diffraction methods were used to investigate the changes in the functional groups and the chemical structures in the wood charcoal. The wood charcoal and original materials were dried at 105°C for 24 h before analysis.

Fourier-transform infrared spectroscopy

The infrared spectra of the wood charcoal and carbonized cellulose were obtained with a FTIR apparatus (FT-IR 7000; Nihon Banko, Japan) using the KBr pellet technique. Charcoal powder of 1–2 mg were mixed with 200 mg KBr, and a pellet was formed by pressing.

X-ray diffraction

The X-ray diffractograms were obtained with a XRD apparatus (RINT 1400; Rigaku Denki, Japan) using Cu-K α radiation. The measurement conditions were as follows: 50 kV tube voltage, 80 mA tube current, and 4°/min scanning speed.

X-ray photoelectron spectroscopy

The XPS spectra of charcoal and original materials were obtained on a XPS apparatus (AXIS-HS-1; Shimadzu/

KRATOS, Japan/England) using MgK α as the photon source. The anode voltage was set at 15 kV and the anode current at 10 mA; the background pressure in the analytical chamber was adjusted to under 10⁻⁸ mmHg. The spectra were referenced by setting 285.0 eV for the C1s aliphatic carbon peak to eliminate the charge effect in the case of wood powder and charcoal carbonized at lower temperatures. The surfaces of the charcoals were etched for 30 s by argon gas before the XPS analysis to exclude the effects of impurities present on the surfaces of the samples. The survey spectra of wood charcoal and cellulose C1s and O1s, respectively were obtained and subjected to background elimination and peak analysis. For peak analysis, the decomposed peak positions were assigned according to the recent literature.^{11,12} The assignments of C1s peak components are shown in Table 1. The peak analysis was performed by means of the peak decomposition to fit a gaussian function by the data-processing program VISION supplied by Shimadzu and KRATOS.

Results and discussion

Change in chemical composites in charcoal investigated by FTIR

The FTIR spectra of the original cellulose and those carbonized at 300, 600, and 800°C are shown in Fig. 1. The infrared spectrum of the charcoal carbonized at 800°C was not as clearly resolved because of the larger absorbance of visible rays of light by charcoal due to its black color. The same tendency was found in the charcoal carbonized at more than 800°C. The spectrum of petroleum pitch becomes obscure because of the increased electrical conductivity of the samples.¹⁰ A carbonization temperature of 800°C is thought to be the limit for the measurement of FTIR spectra of charcoal by the KBr pellet technique.

At first, the O–H stretching vibrational mode at about 3300 cm⁻¹ decreased with increasing carbonization temperature and mostly diminished at a carbonization temperature of 800°C compared to the original material. The C=O mode at about 1700 cm⁻¹ clearly appeared at 300°C. The C=C mode near 1660–1630 cm⁻¹ was weakly detected in the spectra of the charcoal carbonized at 300–600°C. The aromatic mode at about 1600 cm⁻¹ was weak at 600°C.

Based on these results, a decrease in the O–H mode after increasing the heating temperature indicated dehydration

Table 1. Positions and assignments of C1s peak components

Name	Binding type	Binding energy (eV)
C1	Graphite/aromatic	284.6
C2	Aliphatic	285.0
C3	C–OH, C–O–C	286.1
C4	C=O	287.6
C5	COOH	290.1
C6	$\pi - \pi^*$	291.2

The peak positions are those reported by Darmstadt et al.¹¹

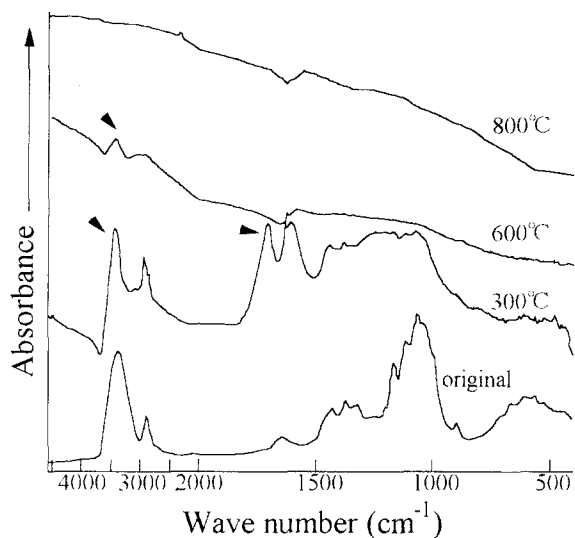


Fig. 1. Fourier-transform infrared spectroscopy (FTIR) spectra of carbonized cellulose
Numbers in the figure indicate carbonization temperatures

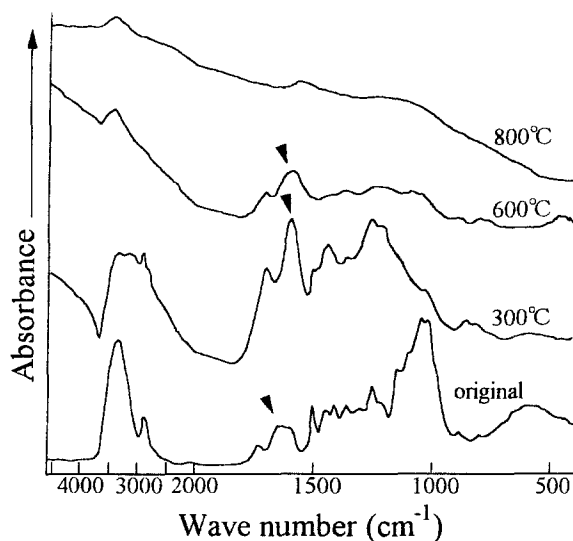


Fig. 2. FTIR spectra of wood charcoal

of the charcoal, which was proved by the formation of a C=O peak that appeared on the charcoal heated at 300°C, but disappeared at 600°C. This sequence suggested that double bonds were formed in the charcoal by dehydrogenation during the carbonization process. These results are in accordance with the carbonization behavior of cellulose described previously.¹³

The infrared spectra of original and carbonized sugi wood are shown in Fig. 2. In the case of the original wood, aromatic absorption originating from lignin¹⁴ was detected at about 1600 and 1510 cm^{-1} . These aromatic modes were also found in the charcoal but moved to a lower wave num-

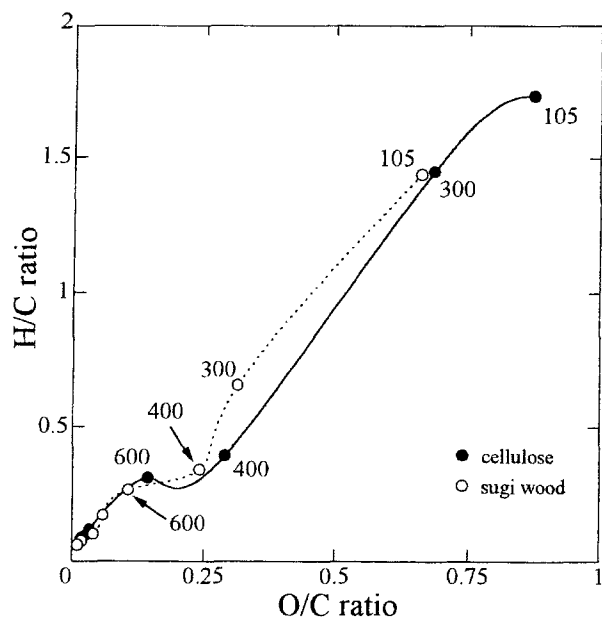


Fig. 3. Krevelen diagram for carbonized materials. Carbonization temperatures are shown near the plots in this diagram

ber with the increase in carbonization temperature. This result suggested that the aromatic mode due to lignin was changed to a different type of aromatic compound by the carbonization. The aromatic outer-vibration mode appeared at about 900–685 cm^{-1} in the charcoal samples after carbonization.

The C=O mode was detected at about 1740 cm^{-1} in original wood due to hemicellulose, although the mode at about 1700 cm^{-1} showed maximum absorbance at a carbonization temperature of 300°C. The C=O mode seemed to be formed by decomposition of cellulose, as shown in Fig. 1. The O–H mode at 3300 cm^{-1} decreased with an increasing carbonization temperature.

The Krevelen diagram was introduced to the data for elemental analysis¹⁵ to describe the changes in chemical structure of the wood charcoal. As shown in Fig. 3, the Krevelen diagram is expressed as H/C ratios of the charcoals versus their O/C ratios. The diagram suggests the types of reaction that occur during the carbonization process.¹⁶ Dehydrogenation began at 300°C and deoxidation at a temperature of 300–600°C. From these results it can be determined that carbonyl groups formed at 300°C because of dehydrogenation. The carbon double bonds or aromatic rings were generated because deoxidation occurred, and the proportion of carbon in the charcoal increased at temperatures of 300–600°C. These results agreed with those from the FTIR spectra. Dehydration progressed at temperatures of 600–800°C. The proportion of carbon atoms increased in the same temperature range, suggesting the beginning of condensation of aromatic rings. In the temperature range just under 800°C the results obtained from this study have something in common with those of Abe et al.¹⁷ and Kishimoto et al.¹⁸

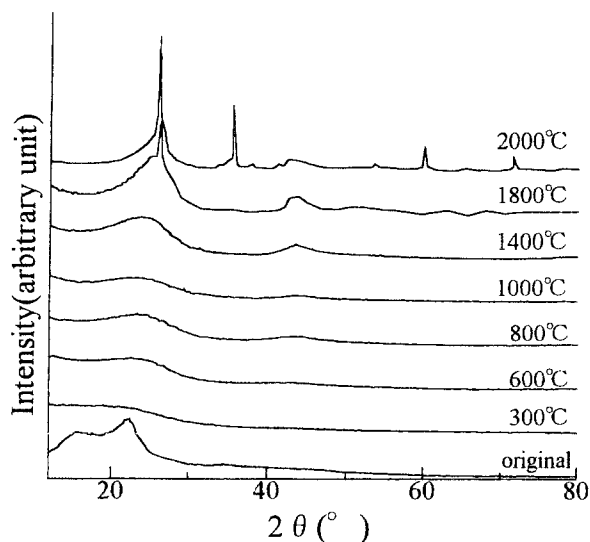


Fig. 4. X-ray diffractograms of wood charcoal

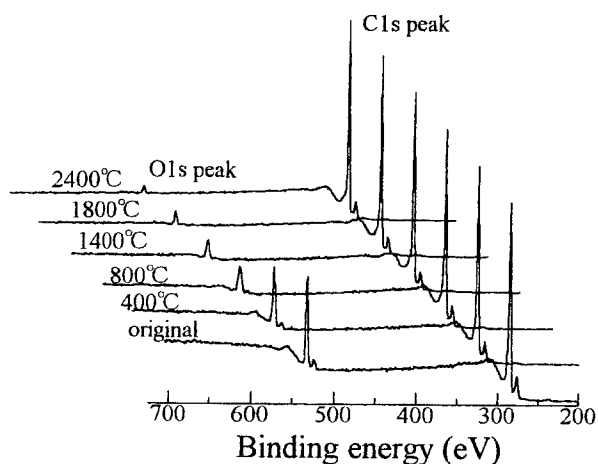


Fig. 5. X-ray photoelectron spectroscopy (XPS) survey spectra of wood charcoal carbonized at various temperatures

X-ray diffraction

X-ray diffractograms of wood charcoal are shown in Fig. 4. Peaks originating from cellulose were detected from original wood. These peaks disappeared when the wood was carbonized even at 300°C, a result that indicated decomposition of the crystal structure of cellulose by thermal decomposition of cellulose. No clear diffraction peaks were detected at temperatures below 1400°C, suggesting no graphitization in the charcoal. The X-ray diffraction pattern changed gradually with the increase in temperature, possibly owing to ultrastructural changes in the charcoal. The sharp peaks that seemed to originate from the graphite crystalline structure appeared in charcoal carbonized at 1800°C and 2000°C.

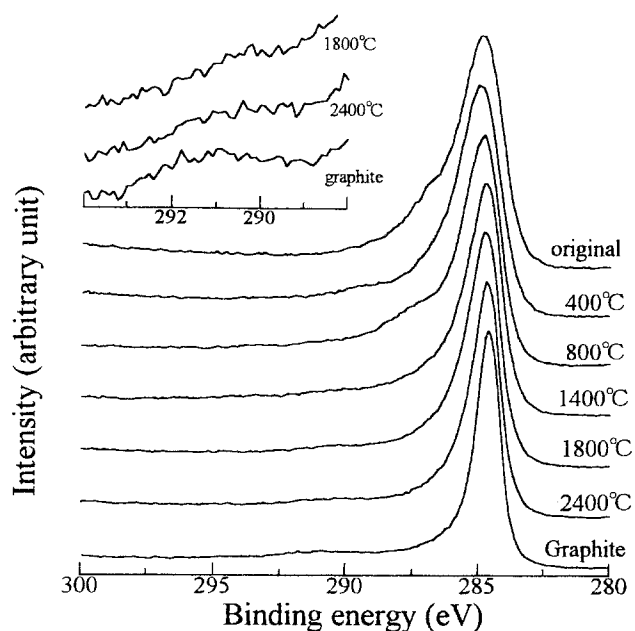


Fig. 6. C1s spectra of wood charcoals carbonized at various temperatures and graphite. The graph at upper left is the magnification around the binding energy 288–294 eV

Charcoal investigated by X-ray photoelectron spectroscopy

The XPS survey spectra of wood charcoal produced from sugi carbonized at various temperatures are depicted in Fig. 5 at a binding energy of 200–700 eV. The C1s (about 285 eV) and O1s (about 532 eV) photoelectron peaks were clearly resolved. Photoelectron peaks originating from other atoms were small, which shows that the charcoal consists of mainly carbon and oxygen. The intensity of O1s peak decreased with higher carbonization temperatures, so the carbon atoms increased against the oxygen atoms.

The C1s spectra were chosen to investigate the chemical structure of charcoal. XPS is sensitive to the state of the samples. A few charcoal samples were influenced by surface oxidation when there was no etching, so etching was undertaken. Because the spectra seldom changed while increasing the etching time, the inner structure of charcoal is represented on the surface after etching. As shown in Fig. 6, the peak width of the C1s spectra of the charcoal carbonized at lower temperatures was broad, and the maximum peak position shifted at a higher binding energy. The C1s spectra tended to shift at the higher binding energy when the carbon atoms were combined with oxygen atoms.

The shape of the C1s spectra of the charcoal carbonized at higher temperatures resembled that of graphite. The small, broad peak around 290–294 eV in graphite and charcoal carbonized at 2400°C was thought to be a plasmon-loss peak or $\pi - \pi^*$ shake-up satellite peak,^{19,20} generated by the existence of numerous π -electrons. It can be said that graphitization occurred when wood was carbonized at 2400°C.

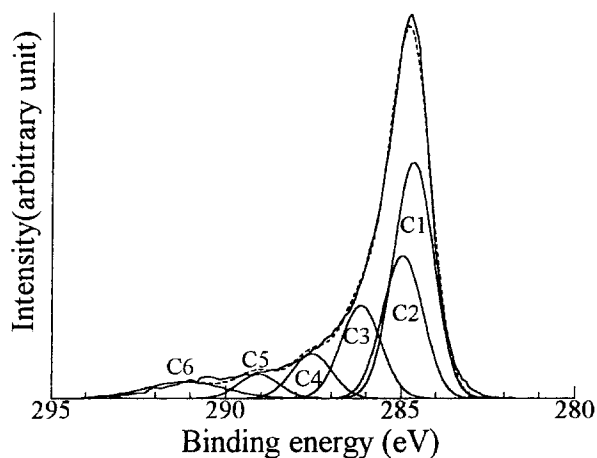


Fig. 7. Example of peak extraction of C1s peak of charcoal (refer to Table 1)

Table 2. Area of C1s peaks of wood charcoal

Carbonization temperature(°C)	Area of the C1s peak (%)					
	C1	C2	C3	C4	C5	C6
Original	23.40	39.86	21.42	12.59	2.69	0.06
300	11.89	48.90	24.31	9.93	3.08	1.74
400	8.82	53.69	21.02	10.09	4.86	1.51
600	19.71	38.56	22.80	12.35	4.38	2.20
700	12.38	60.07	16.68	7.66	3.04	0.14
800	31.00	33.95	15.82	13.01	4.03	2.19
1000	44.66	24.04	15.75	9.24	3.68	2.65
1400	44.94	22.55	16.87	9.61	3.83	2.21
1800	44.21	25.31	16.31	8.52	3.80	1.85
2000	55.06	11.28	18.44	9.29	3.88	2.05
2400	64.77	9.93	15.75	5.39	1.97	2.19

For explanation of C1–C6 refer to Table 1.

Peak extraction

To evaluate the chemical structures of the surface of charcoal, peak extraction was processed to the C1s spectra. All of the C1s spectra were considered to consist of components related to carbon-containing functional groups. The chemical binding state in charcoal can be distinguished by analyzing the components extracted from the C1s spectra. The extracted peaks appeared as in Fig. 7 by curve fitting. In this case the peaks corresponded to those of aromatic carbon, aliphatic carbon, the C=O peak, or the C-OH peak. The areas of the C1s peak components were calculated and are shown in Table 2.

The relation between the carbonized temperature and the aromatic carbons/aliphatic carbons ratio ($C_{\text{aro}}/C_{\text{ali}}$) is represented in Fig. 8. This ratio is thought to be a reflection of the amount of aromatic or condensed aromatic carbons in the charcoal.

The $C_{\text{aro}}/C_{\text{ali}}$ ratio was less than 0.5 at a carbonizing temperature <700°C and rose to about 2.0 at around 1000°C. This value remained almost constant until 1800°C and then

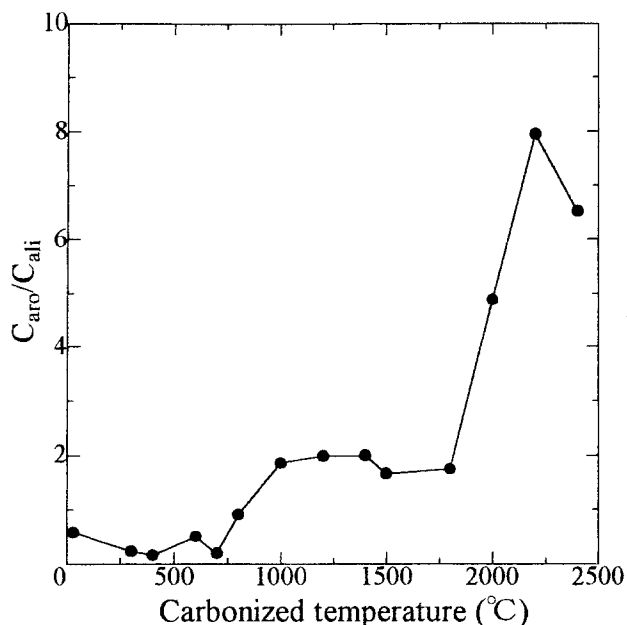


Fig. 8. Relation between carbonizing temperature and the $C_{\text{aro}}/C_{\text{ali}}$ ratio obtained by XPS

rose again to 5.0 at 2000°C. The $C_{\text{aro}}/C_{\text{ali}}$ ratio of graphite was about 20, which was much higher than that for wood charcoal. The rise in the $C_{\text{aro}}/C_{\text{ali}}$ ratio at 800–1000°C is due to formation of some condensed aromatic rings, which may noticeably influence the electrical resistance of the charcoal. Fukuda et al.²¹ suggested that the electrical conductivity of carbon materials is due to condensed aromatic carbons and a few oxygen atoms. Charcoals from various types of wood carbonized at these temperatures have similar chemical structures, so the electrical conductivity of the charcoals is probably the same. In this case, the oxygen atoms may act as a dopant.²² On the other hand, the rise in the $C_{\text{aro}}/C_{\text{ali}}$ ratio at 1800°C was possibly due to the growth in the graphite crystalline structure, which was confirmed by X-ray diffraction of the charcoal.

The components of C3(C-OH), C4(C=O), and C5(COOH), which contained oxygen atoms, gradually decreased with an increasing carbonization temperature. The peaks for C3 and C4 were detected for almost all carbonization temperatures. Apparently, the functional groups in the charcoal decreased with the carbonization temperature, and the proportion of the OH group became comprehensively higher than those of other functional groups as a whole. It was due to the fact that the O1s peak of the charcoal carbonized at higher temperatures was small, even though the functional groups of hydroxyl and carbonyl seemed to be present in the charcoal carbonized at the higher temperatures.

When compared with the results from the FTIR spectra, the basic behavior of the functional groups of charcoal during carbonization can be investigated by means of XPS. For sugi wood, it was found from the C1s spectra of XPS that hydroxyl and carbonyl groups decreased with increasing

carbonization temperature, similar to the results obtained with FTIR, although the difference in carbonyl groups originating from hemicellulose and thermally decomposed wood was not detected by XPS.

In the case of cellulose, the unexpected peak due to carbonyl groups was detected in the XPS spectrum of original cellulose by curve fitting. The peak, which was not as strong, might be due to the effect of etching. It may also be due to the limitation of the algorithm for curve fitting, which leads to a nonexistent peak when peak tailing is distinguished. The peak of carbonyl group was detected in cellulose carbonized at 300°C, but it decreased at 600°C, in accordance with the results from FTIR. The changes in functional groups of charcoal were assumed to be basically determined by means of the peak extraction using XPS.

Conclusions

The carbonization of wood at temperatures below 800°C proceeds as follows. The crystalline structure of cellulose was destroyed, and carbonyl groups were generated at about 300°C, which seemed to be the early stage of carbonization. The disappearance of carbonyl groups and the generation of carbon double bonds and aromatic rings were observed. Dehydration and an increase in the proportion of carbon occurred >600°C with a gradual increase in the condensation of aromatic rings. It was also shown by XPS analysis that the functional groups containing oxygen decreased during the carbonization process. Basically, the results obtained by FTIR were accordance with those of XPS using the curve-fitting technique.

X-ray photoelectron spectroscopy and X-ray diffraction analysis were used to evaluate the chemical structure of wood charcoal carbonized at high temperatures because the FTIR spectra were not clear owing to some limitations, described above. It was revealed by XPS that the proportion of aromatic carbon rose at temperatures of 800–1000°C and 1800°C. The X-ray diffractograms showed sharp diffraction peaks above 1800°C. It was believed that condensation of the aromatic rings began at about 800°C, and the structure of the π -electron system was generated even though it did not attain perfect graphitization. Above 1800°C, the condensed aromatic rings in charcoal changed to graphite in terms of structure. A drastic reduction in the electrical resistivity of charcoal was observed in the sample carbonized at about 800°C in accordance with the change in chemical structure of wood charcoal. It was assumed to be the reason the π -electron system was generated by the condensation of aromatic rings during carbonization. It was also suggested that the electrical conductivity of wood charcoal at room temperature originated mainly from generation of the π -electron system.

Acknowledgments A part of this study was financially supported by Grants for Research Expenses from Kansai Research Foundation for Technology Promotion and by a Grant-in-Aid for Developmental Scientific Research B (no. 03556025) and B1 (no. 06556056) from the Ministry of Education, Science and Culture, Japan.

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