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Quantification of oxygen surface groups on carbon materials via diffuse reflectance FT-IR spectroscopy and temperature programmed desorption

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ABSTRACT

The aim of this investigation is to quantify surface oxygen groups on an activated carbon by combining the results from temperature programmed desorption (TPD) and diffuse reflectance FT-IR spectroscopy (DRIFTS). A commercial activated carbon was oxidized with ozone to form surface oxygen groups. Afterwards the samples were heated in TPD experiments up to 500 °C. The evolved gases were detected and quantified via IR spectroscopy and DRIFT spectra were collected from the heat-treated samples. Simulation of the DRIFT spectra with a set of Gauss functions led to identification of four surface oxygen groups in the range of 1500–1950 cm^{-1}. Specific concentrations of the four groups can be calculated with the conversion factors obtained by combining TPD and DRIFTS information.

1. Introduction

The application properties of carbon materials like activated carbon are influenced by the nature and quantity of their surface groups. For this reason, it is of interest to characterize the single surface groups qualitatively and quantitatively. Several experimental techniques have been applied to analyze oxygen surface groups on carbonaceous materials. These include methods like titration, temperature programmed desorption (TPD) and spectroscopic techniques (e.g. XPS or DRIFTS) [1].

One widely used method for quantification is the so-called Boehm titration that distinguishes the acid surface groups by their different acidity. However, Boehm titration is time-consuming and can be inaccurate in case of materials with small pores [1]. In contrast, temperature programmed desorption (TPD) allows to analyze all surface groups but provides no information about their nature and quantity straightforward. In a number of publications, FT-IR spectroscopy is used for characterization of carbon materials [2–6]. Diffuse reflectance FT-IR spectroscopy (DRIFTS) provides information about the surface and the upper layers of the bulk and different models for quantitative analysis with DRIFTS exist (e.g. Kubelka–Munk model). IR bands with small extinction coefficients are stronger in DRIFT spectra than in comparable transmission experiments. Because of the high self-absorption of materials like activated carbon dilution or KBr pellets are required if transmission FT-IR spectroscopy is applied. Therefore, DRIFTS is particularly suitable with regard to analyze carbon materials. Often results from DRIFTS and TPD are combined. For quantification, generally the TPD profiles of CO and CO_2 are deconvolved to estimate the surface concentrations of each group [7]. The objective of this investigation is to transfer a method for quantification of oxygen surface groups on carbon black [8] upon other carbon materials, e.g. activated carbon. This method allows determination of several oxygen surface groups by TPD and DRIFTS via simulation of the spectra.

2. Experimental

Ozone was used as oxidizing agent to modify the surface of a commercial activated carbon based on hard coal with an internal surface area $>1000\ m^2\ g^{-1}$ (received from CarboTechAC GmbH, Essen). Oxidation was carried out in a stainless steel fixed bed reactor (4.5 cm × 6 cm × 6 cm) attached to an IR spectrometer (FTS 175 C, BIORAD) to analyze the gas phase (CO, CO_2, O_3, H_2O). The path length of the gas cell was 14 cm and gas phase spectra were collected with an optical resolution of 4 cm^{-1}. The fixed bed reactor was equipped with four heating cartridges (per 200 W) and a thermocouple. For oxidation, the reactor was filled with 200 mg of the activated carbon. After drying at 100 °C for half an hour, the activated carbon sample was treated with 4000 ppm ($L\ L^{-1}$) ozone in a N_2/O_2 (1:1.3) stream. Ozone was received from an ozonizer (COM-SD-30, Anseros, Tübingen). The activated carbon used for TPD experiments was oxidized at 60 °C for 3 h (herein after referred to as AC-ox).

DRIFT spectra were collected with a FT-IR spectrometer (FTS 175 C, BIORAD) equipped with a DRIFTS cell developed in-house

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which allows in situ investigations [9]. This cell distinguishes itself through the fact that both the sample and the reference material are in the same gas-proof reaction chamber. The substances are situated in rotatable sample cups which turn into the IR-beam alternately. Either KBr or the unoxidized activated carbon was used as reference material.

The TPD experiments were carried out in the fixed bed reactor mentioned above with the oxidized sample AC-ox that was divided into 10 portions. The samples were heated up to nine different end temperatures (range 100–500 °C, $\Delta T = 50\,°\mathrm{C}$) in a N_2 flow at a heating rate of 10 K min^{-1}. Half an hour after the end temperature was reached, the reactor was cooled down to ambient temperature and an ex situ DRIFT spectrum of the resulting sample was collected (sample was undiluted, optical resolution 4 cm^{-1}). The unoxidized material (AC) was used as reference to receive a straight baseline for subsequent simulation of the spectra. A set of Gauss functions simulates the DRIFT spectra in the region between 1500 and 1950 cm^{-1}. Elemental analysis for N, C and H was carried out with a VarioEL analyzer, O was calculated as difference to 100%.

3. Results and discussion

Depending on the reaction period, activated carbon was obtained in different degrees of oxidation. Fig. 1 shows the ex situ DRIFT spectra of the untreated and oxidized activated carbon with KBr as reference. There are three main peaks in the region between 1000 and 1900 cm^{-1}. A broad one around 1275 cm^{-1}, which is assigned to superimposed C–O stretching originating from e.g. carboxylic acid groups [10]. Moreover, there is a peak at 1602 cm^{-1} resulting from polyaromatic C=C stretching vibrations. It is known that carbonyl groups conjugated with the aromatic system enhance these vibration modes. Therefore, the peak at 1603 cm^{-1} is considered as a measure of highly conjugated carbonyl/quinone groups [6]. Furthermore there is one peak at 1780 cm^{-1} showing a shoulder at 1855 cm^{-1}. These wavenumbers are associated with C=O stretching in for instance anhydrides and carboxylic acids [6,8]. Around 3300 cm^{-1} another very broad band appears which is assigned to C–OH stretching modes [11]. As expected, all of the mentioned peaks increase with proceeding oxidation. Further investigations were focused on the peaks in the region between 1500 and 1950 cm^{-1}.

During temperature programmed desorption the sample evolves CO and CO_2 (Fig. 2). Around 150 °C both CO and CO_2 release show a peak resulting most likely from decomposing carboxylic acid and anhydrides [8]. CO evolving at such low temperatures was not expected as it is reported in the literature that CO evolves from temperatures higher than 400 °C [5,6]. Nevertheless, IR spectroscopy as well as MS analysis (not shown here) independently showed CO evolving at the mentioned temperatures. There is also some literature that reports CO evolution around 237 °C [4,7]. With increasing temperature, the CO_2 decreases whereas CO slightly increases from 400 °C due to decomposition of carbonyl groups [4]. The elemental analyses of the untreated (AC), the oxidized activated carbon (AC-ox) and the samples from TPD are listed in Table 1. From this it follows that the content of oxygen was increased 14.5% (g g^{-1}) by oxidation. By TPD the oxygen content decreases but at 500 °C there is still about 4% (g g^{-1}) more oxygen in AC-500 than in AC.

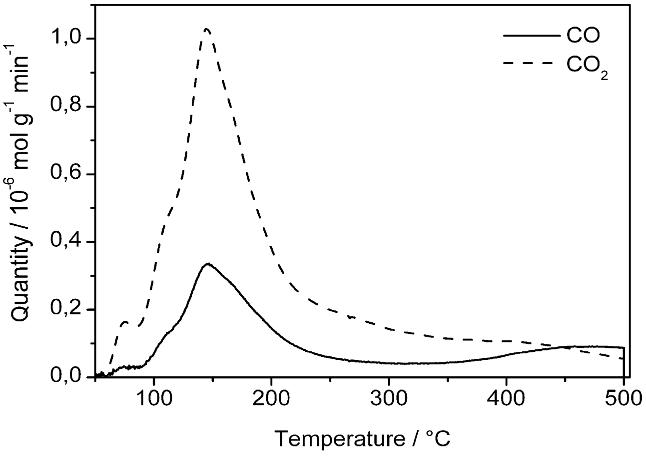

Fig. 2. Quantity of CO and CO_2 evolved from sample AC-ox during temperature programmed desorption (heating rate = 10 K min^{-1}).

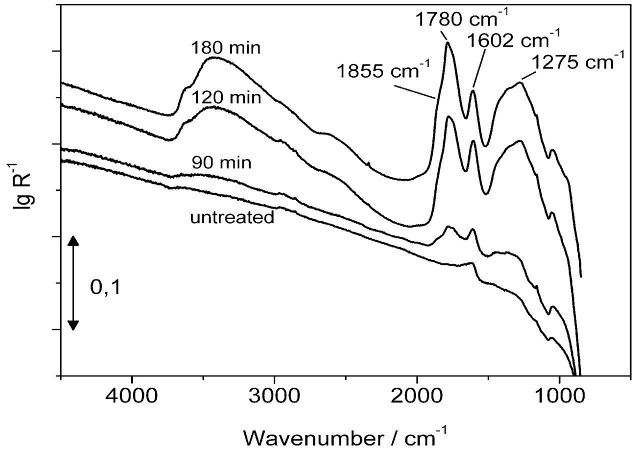

Fig. 1. Ex situ DRIFT spectra of untreated activated carbon and activated carbon oxidized with 4000 ppm (L L^{-1}) ozone at 60 °C with KBr as reference.

The ex situ DRIFT spectra of AC-ox and the nine samples received by TPD experiments are depicted in Fig. 3 with AC as reference. The peaks show different decomposition kinetics while heating up. The band at 1602 cm^{-1} first shows no significant change until 350 °C and then reduces slightly. In contrast, the peak at 1780 cm^{-1} decreases constantly with increasing temperature whereby the former shoulder at 1855 cm^{-1} is emphasized, especially from 150 to 350 °C.

As reported in the literature, IR spectra can be simulated with different distribution functions. Usually Gauss or Lorentz functions are used. For spectra of solids also product or sum functions of Lorentz and Gauss are applied [12]. Simulation of multiple-band spectra is accompanied with some difficulties. Beside the problems due to overlapping bands, the main questions to answer are how many components are involved and how the single functions are shaped [13]. The 10 DRIFT spectra (Fig. 3) were simulated with a set of Gauss functions (Fig. 4). The least number of single Gauss functions that reproduce the original spectra is four. However, this model would not be in accordance with the chemical background as explained below. Literature describes that anhydrides appear in IR spectra as a doublet peak with one at 1750–1790 cm^{-1} and the other at 1830–1880 cm^{-1} [6]. Lactones are supposed to show a single peak around 1750 cm^{-1}. Dauben and Epstein examined the IR intensities of the doublet peak for various anhydrides. It is reported that in case of cyclic anhydrides the peak at lower wavenumbers is stronger than the one at higher wavenumbers [14]. Therefore, a simulation was performed with five single Gauss functions (double band for anhydride) on condition that the anhydride band at 1830–1880 cm^{-1} is weaker than the one at lower wavenumbers (Fig. 5).

The integral associated with the peak at 1602 cm^{-1} decreases slightly from 100 °C. The integral of the band at 1765 cm^{-1} decreases rapidly from 100 °C. At temperatures above 200 °C the decrease is extenuated and at 350 °C the integral is nearly zero.

Table 1
NHC-amounts from elemental analysis of AC, AC-ox and the samples received from TPD (100–500 °C). The amount of O is calculated as the difference to 100%.

	Elemental analysis (%) ($g\,g^{-1}$)										
	AC	AC-ox	100 °C	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C
N	0.28	0.34	0.46	0.42	0.36	0.35	0.33	0.29	0.37	0.46	0.42
C	76.99	62.37	62.74	65.78	67.60	67.67	68.43	69.54	70.26	71.92	72.90
H	1.04	1.10	1.11	0.80	0.78	0.75	0.80	0.71	0.72	0.70	0.67
O	21.69	36.19	35.85	33.08	31.26	31.23	30.44	29.46	28.65	26.92	26.01

The integral of the 1740 cm^{-1} peak is constant up to 350 °C and then decreases whereas the peak at 1855 cm^{-1} already does so from 300 °C. The peak at 1792 cm^{-1} shows an increase of integral value from 150 to 300 °C and then decreases. Based on the development of the integral of each separated IR band (Fig. 5) and the specific decomposition temperatures known from the literature, the peaks are assigned as follows. The peak at 1602 cm^{-1} belongs to the carbonyl groups which decompose to CO. Carboxylic acid groups appear in the DRIFT spectrum at 1765 cm^{-1} and decompose already from 100 °C to give CO_2. Another possible explanation for the decrease is that two neighboring carboxylic acid groups condense to give an anhydride group. According to the literature, the band at 1740 cm^{-1} would represent the lactones which evolve CO_2 at temperatures higher than 350 °C. The double band of anhydrides is located at 1792 and 1855 cm^{-1}. The increase of the 1792 cm^{-1} peak from 150 to 300 °C can be correlated with the formation of anhydride groups by condensation of two carboxylic acid groups. At temperatures above 300 °C, the anhydrides decompose to CO and CO_2. The weaker anhydride band at 1855 cm^{-1} does not show the same obvious increase at 150 °C but also reduces above 300 °C.

To quantify the four groups observed in this work a formation and decomposition mechanism, like the schema in Fig. 6, needs to be set up. Acting on the assumption that the concentration on the surface is proportional to the integral value of the group, the mass balance has been solved by applying the integral values and the quantities of CO and CO_2 evolved during TPD. With the resulting conversion factors and the integral values, the specific concentrations can be determined as shown in Table 2. For anhydrides the integral value of 1792 cm^{-1}, which showed the expected anhydride behavior, was applied to the mass balance.

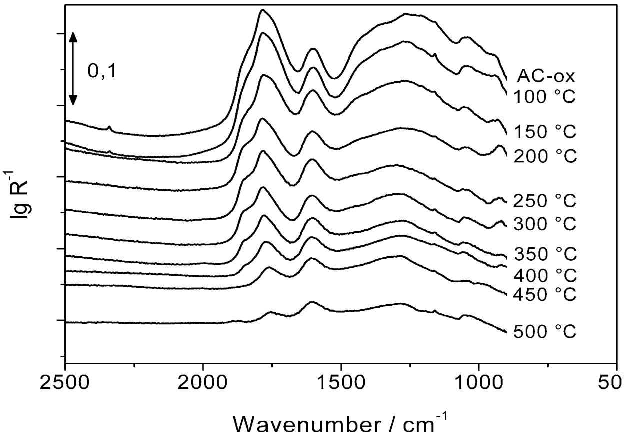

Fig. 3. Ex situ DRIFT spectra of AC-ox and the nine samples received from TPD experiments of AC-ox with the unoxidized activated carbon as reference.

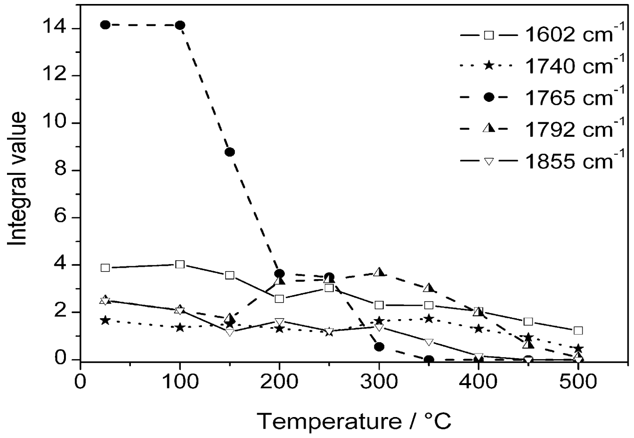

Fig. 5. Integral values of the five peaks received from simulation of the DRIFT spectra in Fig. 3 with five single Gauss functions (double band for anhydride).

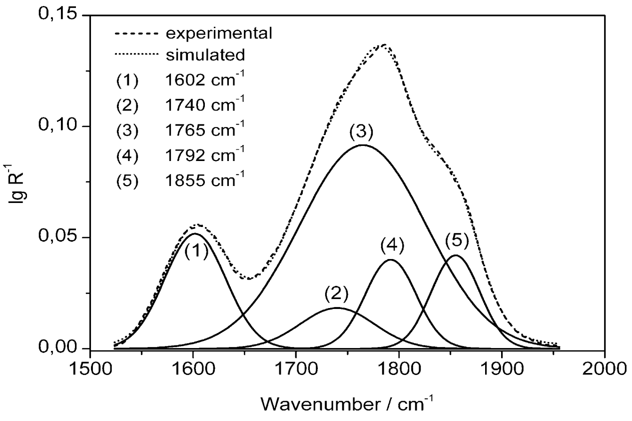

Fig. 4. Example for simulation of a DRIFT spectrum with a set of five Gauss functions located at 1602, 1740, 1765, 1792 and 1855 cm^{-1}.

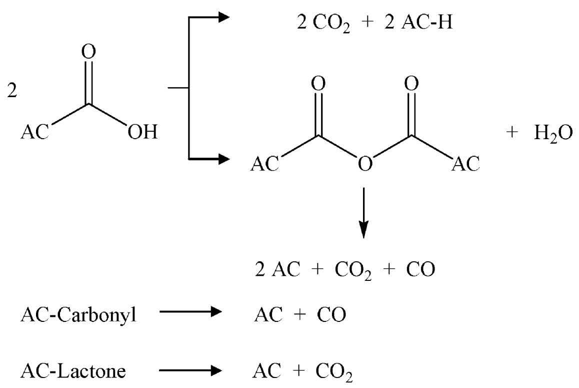

Fig. 6. Scheme of the formation and decomposition mechanism of four oxygen surface groups on activated carbon, AC = activated carbon.

Table 2
Identified surface oxygen groups with their peak position in DRIFT spectra, decomposition temperatures and evolved gases thereby and the conversion factors for calculation of the specific concentrations. Simulation of the DRIFT spectra was carried out with five single Gauss functions. The specific concentration was calculated exemplarily for AC-ox.

Group	Peak (cm^{-1})	Evolved gases	Decomposition temperature (°C)	Conversion factor ($mmol\ g^{-1}$)	Specific concentration ($mmol\ g^{-1}$)
Carbonyl	1602	CO	400	0.132	0.51
Carboxylic acid	1765	CO_2	100	0.245	3.47
Lactone	1740	CO_2	350	0.294	0.49
Anhydride	1792[a]	CO, CO_2	150	0.217	0.54

[a] Double band for anhydrides at 1792 and 1855 cm^{-1}. The single function with the higher intensity was chosen for the determination of the conversion factors.

4. Summary

An activated carbon was oxidized with ozone and TPD experiments were conducted. DRIFT spectra showed several peaks in the investigated region between 1500 and 1950 cm^{-1}. The collected ex situ DRIFT spectra after each end temperature in TPD showed that the peaks decrease with different rates. The DRIFT spectra were simulated with a set of five single Gauss functions. Four surface oxygen groups in the region between 1500 and 1950 cm^{-1} were identified by the combination of the results of TPD and DRIFTS. The specific concentration of each group can be calculated from the integral and the conversion factor obtained from solving the mass balance. The advantage of the method described here is that in the end it would enable the quantification of the surface oxygen groups by just one DRIFT spectra.

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