



Non-linear thermogravimetric mass spectrometry of carbon materials providing direct speciation separation of oxygen functional groups



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ABSTRACT

Thermogravimetric mass spectrometry (TG-MS) is an established way to analyze oxygen containing surface functional groups of carbon materials. Thermal stabilities and structures of functional groups influence their decomposition temperatures and products (CO, CO₂). In this work, a non-linear procedure with isothermal steps is presented enabling a separation of functional groups by different decomposition temperatures. Nitrosulfuric acid functionalized carbon materials like multi-walled carbon nanotubes (MWCNT) and graphite were used to design the temperature program. Comparative studies of linear and non-linear heating experiments in argon and hydrogen containing atmosphere were performed to state the benefits and limits of both methods. The distinct advantage of non-linear thermal analysis is demonstrated by an application-oriented experiment where only selected functional groups are consumed.

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1. Introduction

Multi-walled carbon nanotubes (MWCNT) are highly desired materials for numerous applications. Due to their unique structure they combine graphitic properties like high conductivity, thermal and mechanical stability with high surface area (250 m²/g) [1–4]. Properties of the MWCNT are strongly linked to the amount and kind of functional groups on the surface [5–7]. With an increasing amount of functional groups the conductivity and stability of MWCNT will unavoidably change. In catalysis, MWCNT are often used as support materials for small active particles [1,8]. The functional groups on the surface of the supporting MWCNT can influence the stability of the compound material. Hence, particle attachment and solubility will be influenced by the surface properties. In some cases functional groups show catalytic activities by themselves [9,10]. To describe the interaction between metal catalysts and functional groups, or to determine the catalytic activity of the carbon material itself, it is necessary to qualitatively and quantitatively identify functional groups and describe the changes to such groups before and after their use in a catalytic reaction [11,12]. Post-analysis therefore allows one to monitor the chemical

changes, and to identify functional groups that are consumed or produced during a reaction. Several approaches are used to overcome this challenge. For instance titration methods use the different pK_a values of functional groups for the quantification. The conversion of functional groups, diffusion and acid residuals of MWCNT pre-treatments often impede a former characterization of functional groups [13]. Catalytic tests like the oxidation of isopropanol are used to generate sum parameter where acidic and alkaline functional groups are separated. However, the reaction temperature applied during this catalytic test already changes the composition of functional groups and influences the quantification [14].

Thermogravimetric mass spectrometry is a common way to analyze surface functional groups on carbon materials [15,16]. During the thermal treatment, oxygen-containing functional groups, depending on their structure, decompose into CO₂ or CO. Traditionally, TPD approaches use solely heating rates in argon atmosphere with a linear temperature program. Results gained out of these experiments do not enable the exact determination of the decomposition temperature of different functional groups. Overlapping signals due to the decomposition of multiple functional groups with similar decomposition temperatures hinders an exact determination of decomposition temperature [17–20]. Recently, thermal stabilities of different surface functional groups were determined by a combination of temperature programmed

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desorption (TPD), X-ray Photoelectron Spectroscopy (XPS), titration, and catalytic test reaction experiments [21]. Due to the combination of these methods an exact determination and assignment of the decomposition temperatures of functional groups, where maxima of the decomposition products are analyzed, was possible (see Table 1). Even if the decomposition temperatures of the functional groups have already been discussed the problem of overlapping signals during TPD measurements still exists, and prohibits differentiation of functional groups. For a quantitative analysis of functional groups via TPD, a separation during the decomposition process is required.

The present work focuses on separating the decomposition products of functional groups during TPD measurements based on the observations summarized in Table 1. To accomplish this, we used a non-linear temperature program procedure. This method is now referred to as an isothermal temperature program. Due to the insertion of isothermal steps during the heating process, the overlay between different desorption process from chemically different functional groups can be avoided by completing each desorption process prior to increasing the decomposition temperature. The temperatures of these isothermal steps were determined by analyzing the peak shape of the individual ion currents. Moreover, literature values were used to confirm the temperatures determined for the separation of functional groups [19–26]. Applying an isothermal temperature program during the TPD analysis of carbon materials affords the following benefits:

- Isolation of different functional groups due to thermal separation
- Identification of decomposition temperature ranges for different functional groups
- Particular detection of decomposing products of functional groups with different decomposition temperatures
- Detection of interconversion of functional groups before and after reaction conditions (e.g. consumption, formation, conversion etc.)

In addition to the influence of isothermal steps on the detected signals of decomposition products, the influence of different heating rates on the decomposition was investigated. Thereby, the influence of kinetic hindrances on the CO_2^+ and CO^+ ion currents was investigated. The shapes of the ion currents were not affected by the heating rate and shoulders appearing during the analysis are related to different functional groups.

2. Materials and methods

2.1. Functionalization of carbon materials

Graphite (Merck Millipore) as well as MWCNT produced from Shangdong Dazhang Nano Materials Co. were treated with nitro-sulfuric acid (vol% ratio: 1:1; nitric acid 65%: sulfuric acid 98%) to

create oxygen containing functional groups on the surface of the MWCNT. The procedure of functionalization is described in detail elsewhere [27]. Briefly 10 g of carbon material was mixed with 500 ml of acid. The mixture was heated to 105 °C and stirred for 4 h. Afterward, the modified carbon materials were filtered and residuals of acid were washed out over several hours in a washing cell. The oxidized carbon was dried in a vacuum-oven at 80 °C for 12 h. To test the applicability of the developed temperature program two commercially available graphitic reference materials, active char and Vulcan XC 75R, were also analyzed. These materials were not pre-treated before analysis.

2.2. Thermal analysis procedure

Thermal analysis was performed using a STA 449 F3 Jupiter[®] QMS4 setup from Netzsch with an argon gas flow of 70 ml/min. Isothermal steps were inserted during thermogravimetric mass spectrometry (TG-MS) analysis to separate functional groups with different decomposition temperatures. The optimum temperature of the implemented isothermal step was judged by the peak shapes of both CO^+ and CO_2^+ signals. Heating rates were varied between 10 K/min and 50 K/min. Based on the investigated results a heating rate of 20 K/min was applied in-between the isothermal steps to avoid overheating while maintaining satisfactory signal intensities, whereas a heating rate of 50 K/min was chosen after the last isothermal step, due to higher signal intensities. Reproducibility was confirmed by three iterations.

2.3. Atomic layer deposition

A commercial atomic layer deposition (ALD) setup (Savannah S200, Ultratech) was used to deposit vanadium oxide on the functionalized MWCNT. Vanadium(V) triisopropoxide (CAS: 5588-84-1, Sigma-aldrich) precursor was heated to 70 °C and exposed for 0.5 s to the acid pre-treated MWCNT. This procedure was repeated for 250 cycles, respectively. Organic residuals of the precursor were purged after each cycle using water pulses of 0.5 s. The temperature of the reaction chamber during the process was held constant at 150 °C.

3. Results and discussion

3.1. Determination of isothermal steps

Thermal decomposition of oxidized carbon materials combined with simultaneous detection of released gaseous products enables the determination of different thermal stabilities of functional groups. To ensure a reliable analysis, the decomposition of surface functional groups at different temperatures needs to be independent of gas transport effects. Therefore, comparison of MWCNT, as representative of high surface materials with a surface area of 239 m²/g and a mesoporous character was compared with graphite, as nonporous material with a surface area of 20 m²/g. Non-porous MWCNT forms bundles due to agglomeration, corresponding empty spaces between MWCNT provides a mesoporous character of these samples [28]. Specific surface areas were determined by N₂ sorption experiments and analyzed by Brunauer-Emmet-Teller (BET) theory showing type II hysteresis for graphite and type IV for MWCNT (supporting information S1). Hence, both materials show similar behavior of relatively weak adsorbent-adsorbate interactions with molecular clustering at higher p/p⁰, and subsequent pore filling in the case of MWCNT.

Different heating rates during the thermal analysis were applied to investigate how heating width affects peak width, position and intensity of the detected CO_2^+ and CO^+ signals of the two

Table 1
Overview of decomposition temperatures of functional groups in carbon structures from Ref. [21].

Functional group	Temperature [°C]	Detected species
Carboxyl	275	$\text{CO}_2 + \text{H}_2\text{O}$
Anhydride	435, 460	$\text{CO}_2 + \text{CO}$
Lactone	650	CO_2
Phenol	735	CO
Ether	735	CO
Carbonyl/ Quinone	920	CO

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