The High-Temperature Acidity Paradox of Oxidized Carbon: An in situ DRIFTS Study

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Until now, oxygen functionalized carbon materials were not considered to exhibit significant acidity at high temperatures, since carboxylic acids, the most prominent acidic functionality, are prone to decarboxylation at temperatures exceeding 250 °C. Paradoxically, we could show that oxidized carbon materials can act as highly active high-temperature solid acid catalysts in the dehydration of methanol at 300 °C, showing an attractive selectivity to dimethyl ether (DME) of up to 92% at a conversion of 47%. Building on a tailor-made carbon model material, we developed a strategy to utilize in situ DRIFT spectroscopy for the analysis of carbon surface species under process conditions, which until now proofed to be highly challenging due to the high intrinsic absorbance of carbon. By correlating the catalytic behavior with a comprehensive in situ DRIFTS study and extensive post mortem analysis we could attribute the high-temperature acidity of oxidized carbons to the interaction of thermally stable carboxylic anhydrides and lactones with nucleophilic constituents of the reaction atmosphere e.g. methanol and H₂O. Dynamic equilibria of surface oxides depending on reaction atmosphere and temperature were observed, and a methyl ester, formed by methanolysis of anhydrides and lactones, was identified as key intermediate for DME generation on oxidized carbon catalysts.

Introduction

Due to a unique set of favorable properties, carbon materials are widely applied as catalyst supports or catalysts themselves in various transformation processes. In this context, high specific surface areas, tunable pore structure and surface chemistry, chemical inertness in a wide range of conditions as well as high thermal and electrical conductivities render carbon the material-of-choice for a variety of catalytic applications. Transformations involving carbon materials reach from energy conversion processes (e.g. fuel cell,[1] electrochemical water splitting[2]) over hydrogenation (e.g. catalyst supports for Fischer-Tropsch-Synthesis[3] and dehydrogenation reactions (e.g. catalysts for the dehydrogenation of ethyl benzene[4–6] and alcohols[7–9]), all the way to acid-base catalysis. Concerning acid catalysis, extensive work has been carried out focusing on metal-free, solid acid catalysts obtained by functionalization of carbon materials with heteroatoms such as O, S or P.[8] From a technical point of view, especially O functionalized carbons represent appealing solid acids, since established oxidation processes allow functionalization to be carried out on an industrial scale, achieving high densities of surface groups. However, O functionalized carbons are widely considered inferior solid acid catalysts, since they are limited to mild reaction conditions (liquid phase, T < 200 °C) due to the immediate decarboxylation of carboxylic acids at higher temperatures.

Paradoxically, in context of the carbon catalyzed oxidative dehydrogenation (ODH) of alcohols it was recently discovered that O functionalized carbons can be active solid acids at high temperatures, catalyzing gas-phase etherification, esterification and dehydrogenation reactions at temperatures well above 300 °C. For instance, the dehydrogenation of ethanol over carbon catalysts in presence of O₂ yielded ethyl acetate, ethylene and diethyl ether[6,10] as prominent side products, while the formation of various butenes was observed during the ODH of n-butanol over multi-walled carbon nanotubes (MWCNTs).[11] Strikingly, dimethyl ether (DME) was indeed observed as the main product of the conversion of methanol (MeOH) over MWCNTs in presence of oxygen at 320 °C.[12]
Since especially DME is a promising candidate for the application as a sustainable, synthetic diesel fuel and represents an important intermediate in a hypothetical methanol-based circular economy for the production of various hydrocarbons, exploring high-temperature-acidic carbon materials as catalysts for DME production is of high interest. However, in order to enable a targeted catalyst design, identification of the responsible acidic centers as well as comprehension of the underlying mechanism of their formation are a prerequisite.

In this context, in situ analysis of carbon surface oxides appears to be the strategy-of-choice, but has so far only been applied sporadically in form of in situ titration and near ambient pressure XPS \(^{[4,7,11]}\). While in situ titration (selective poisoning of active centers) is a powerful strategy to quantify active sites and deduce reaction pathways, it is based on chemical modification of the carbon surface and simultaneously critically dependent on the selectivity of the chosen catalyst poison. Near ambient pressure XPS can provide a large amount of useful information, whereas it is limited to reactant pressures of a few millibars, and the differentiation of chemically similar surface oxide species provides a challenge.

Among other methods, applying diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for the in situ analysis of oxygen surface groups on carbon would offer the advantage of being able to operate at process conditions in terms of pressure, temperature as well as atmosphere, and the measurement itself does not influence the sample composition. However, DRIFTS analysis of carbon surfaces proves to be highly challenging, since low signal-to-noise ratios caused by the high intrinsic absorption of carbon materials severely impede a meaningful application. In consequence, except for the early works by Meldrum et al., who investigated the influence of several gaseous reactants on the carbon surface oxide ensemble, in situ DRIFT spectroscopy has not been adopted for analysis of carbon materials under process conditions since.\(^{[13]}\)

We recently developed a novel polymer-derived graphitic carbon (PDC) dehydrogenation catalyst, that showed a similar mass based catalytic performance compared to carbon nanotubes but achieved space time yields one order of magnitude higher than a MWCNT benchmark.\(^{[6]}\) Closely related to this novel graphitic catalyst, we recently prepared an amorphous carbon, using the identical polymer system as carbon precursor. Hydrothermal oxidation of this amorphous model carbon (AMC) to high oxygen loadings allowed the efficient application of DRIFT spectroscopy for the examination of carbon surface oxygen functionalities, circumventing the problems associated with low signal-to-noise ratios due to the high intrinsic absorption of carbon materials.\(^{[13]}\) Enabling a meaningful interpretation of the spectra despite severe signal overlap of individual surface oxides, we succeeded in the synthesis of adequate reference materials via selective O-functionalization of AMC with carbonyl groups, carboxylic acids, carboxylic anhydrides and lactones.\(^{[13,14]}\)

In this work we want to build on these extensive preliminary efforts and examine the high temperature acidity of O-functionalized carbons by studying the MeOH conversion over a graphitic polymer-derived carbon and correlate the results with the structural information from in situ DRIFTS (Scheme 1). Moreover, the study is accompanied by an extensive post mortem characterization of the carbon surface chemistry of the utilized materials.

**Results and Discussion**

The catalytic conversion of MeOH over oxidized, graphitic, polymer-derived carbon (O-PDC, detailed characterization

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**Scheme 1.** Examination of MeOH conversion over carbon catalysts: correlating the catalytic behavior of a graphitic carbon ODH catalyst to results of an in situ DRIFTS study on a closely related amorphous model carbon.
published elsewhere[6] served as starting point for the examination of the high temperature acidity of carbon materials. MeOH conversion over O-PDC at 300 °C in presence of oxygen proceeds via an induction period of roughly 10 h, after which a catalytic steady state is reached. Over 32 h time on stream, dimethyl ether (DME), formaldehyde (FA) as well as small amounts of CO₂ are detected as reaction products (Figure 1a). Steady state MeOH conversion was found to be 44%, with a selectivity to the main product DME amounting to 69%, to the partial oxidation product FA to 28%, while the total oxidation product CO₂ accounted for 3%. The catalytic activity as well as the selectivity of O-PDC matches the catalytic performance reported in the literature for MeOH conversion in presence of O₂ over MWCNTs quite well.[7]

While the active site for oxidative dehydrogenation reactions, e.g. for formation of FA, has been identified as ketonic carbonyl groups and was examined (also using substrates other than MeOH) extensively,[4,7,11,15] the active site for high-temperature acid-base catalysis has been studied to a lesser extent, with thermolabile carboxylic acid groups (decarboxylation occurs at T > 240 °C)[16] being discussed as possible candidates.[7] Deconvolution of the CO₂ emission profile of temperature programmed desorption (TPD) prior and after catalytic testing of O-PDC shows a significant decrease in the concentration of carboxylic acids for the spent catalyst (from 227 μmol g⁻¹ for O-PDC (oxidized in synthetic air at 380 °C for 72 h) to 124 μmol g⁻¹ for the catalyst after 20 h TOS in presence of O₂) (Figures S1–S3). However, minor CO₂ emission remains, indicating the presence of carboxylic acid groups at low concentration. Boehm titration proved to be impractical for the post mortem analysis of the graphitic O-PDC, since the combination of low oxygen loading and low sample amount available of spent catalysts lead to error intervals of the same order of magnitude as the determined base consumptions. These low concentrations of carboxylic acids and therefore also the high-temperature acidity could be explained by a hypothetical “equilibrium” between the fast thermal decomposition of carboxylic acids at 300 °C and their regeneration via oxidation of the carbon matrix in presence of gaseous O₂.

However, this hypothesis relying on fast oxidative regeneration of carboxylic acids as active centers is contradicted by MeOH conversion over O-PDC at 300 °C in absence of O₂ (Figure 1b), whereas the DME formation rate initially increases significantly (from 3.7 to 5.0 μmol min⁻¹). However, over the course of 20 h time on stream, a slow deactivation can be observed in absence of O₂, with MeOH conversion decreasing from 47% to 39%, while the DME selectivity remains steady at 92%. Since the rate of FA formation remains constant over the...
experiment, the loss of catalytic activity appears to be associated with the loss of acid/base active sites. Deconvolution of the TPD CO\(_2\) emission profile of O-PDC after 20 h TOS in absence of O\(_2\) revealed a loss of all CO\(_2\) evolving surface oxides (–28% for carboxylic acids, –11% for anhydrides and –39% for lactones) compared to the spent catalyst after 20 h TOS in presence of oxygen (Figures S1–3).

To investigate the thermal stability of acidic centers, the O-PDC catalyst was twice exposed to a temperature of 500 °C for 1 h, once in inert gas flow and once in a flow of 1.5 vol-% MeOH in He, while monitoring catalytic performance (Figure 1c). It is clearly evident that the first thermal treatment in inert atmosphere did not exhibit any significant impact on the active sites of DME as well as FA formation (MeOH conversion 54% prior vs. 53% after; selectivity to formaldehyde 24% prior vs. 26% after; to DME 72% prior vs. 69% after). While this behavior was anticipated for the formation of formaldehyde (ketonic carbonyl groups as active sites are stable to temperatures of up to 800 °C),\(^*\) in case of DME formation, the obvious high-temperature stability of the active site appears clearly opposes the hypothesis that carboxylic acid groups are solely responsible for the high temperature acidity of O-PDC. The second exposure of O-PDC to 500 °C was conducted in presence of MeOH, and it becomes obvious that the otherwise temperature tolerant acid/base active sites are not stable in presence of MeOH (Figure 1c). Initially, during the heating phase, the MeOH conversion increases strongly from 51% at 300 °C to 76% at 440 °C and decreases steeply afterwards down to only 10%, until it slowly recovers when O\(_2\) is reintroduced at 300 °C. The selectivity to DME follows a similar trend, passing through a maximum with increasing temperatures followed by a steep decline to <10% and a slow recovery after re-exposure of the catalyst to oxygen. It should be noted at this point, that the slow regeneration of the active acidic site(s) after exposure to 500 °C in presence of MeOH, which does not reach completion even after 10 h TOS, further contradicts the hypothesis that fast regeneration of carboxylic acids by O\(_2\) plays a decisive role in MeOH dehydration over oxidized carbon. The active site for FA formation appears not to be affected by the heat treatment in presence of MeOH, as the rate of FA formation remains nearly identical prior and after exposure to 500 °C (3.3 vs. 3.4 μmol min\(^{-1}\) in absolute terms and 13.7% vs. 13.1% in terms of yield). In consequence, the increased selectivity to FA appears to be solely related to the decomposition of acid/base active sites and the resulting decline in DME formation rate.

In light of the evidence, that the reaction atmosphere itself appears to influencing the stability of active acidic sites, \textit{in situ} DRIFTS experiments in various atmospheres were carried out. For this purpose, the amorphous model carbon with high oxygen loading (O-AMC, 31.9 wt-% O) is employed, in order to provide enough “contrast” between the highly absorbing carbon matrix and the carbon surface oxides of interest (textural and structural properties of AMC have been described elsewhere\(^*\)). The high intrinsic absorbance of the carbon samples required compromising between signal-to-noise ratio and time resolution, whereas an integration time of 15 min was necessary for reaching an adequate signal-to-noise ratio. In this context, temperatures limited to 260 °C were identified as ideal, since this allowed thermal decarboxylation of carboxylic acids, while slow MeOH conversion rates ensured that relevant surface processes were slow enough to be observed within the limited time resolution of the \textit{in situ} DRIFTS experiments.

In this context, the oxidized amorphous model carbon (O-AMC) showed a MeOH conversion of 3% with a selectivity of 50% for DME at a temperature of 250 °C (Figure S4). For the initial in situ DRIFTS experiments, O-AMC was reduced with LiAlH\(_4\) (yielding the reduced amorphous model carbon, R-AMC) (Scheme 2). R-AMC does not exhibit any carbonyl absorption (Figure S5), and develops a distinct carbonyl band upon contact to oxidizing atmospheres, which subsequently allows a facile analysis. In terms of atmosphere, the influence of oxygen in combination with MeOH and H\(_2\)O as a major coproduct were investigated in a temperature range between 140 and 260 °C.

Prior to the \textit{in situ} DRIFTS experiments, temperature programmed oxidation and isothermal thermogravimetric analysis in synthetic air at 250 and 300 °C for 12 h each was carried out, showing that the oxidation resistance of the amorphous O-AMC suffices for the \textit{in situ} DRIFTS experiments (Figure S6a and S6b).

The \textit{in situ} DRIFTS experiments were carried out by using R-AMC prior to the experiment as the reference, recording of spectra was started upon oxygen exposure. In consequence of the oxidizing atmosphere, a fast increase in carbonyl absorption between 1700 and 1900 cm\(^{-1}\) could be detected, with a typical experiment depicted in Figure 2a.

The carbonyl band was subsequently analyzed by mathematical deconvolution, utilizing Gaussian functions and carefully constrained ranges for both absorption maximum and FWHM of the individual surface oxide species (described in detail in the supporting information). The absorption maxima for carbonyl groups (1742 cm\(^{-1}\)), carboxylic acids (1758 cm\(^{-1}\)), lactones (1771 cm\(^{-1}\)) and anhydrides (1792 cm\(^{-1}\) and 1852 cm\(^{-1}\)) were derived from our previous works that focused specifically on the development of carbon reference materials for DRIFTS.\(^{[13,14]}\) In this context, carbon reference materials selectively functionalized with carbonyl groups, carboxylic acids, lactones and anhydrides were synthesized and evaluated, utilizing exactly the same amorphous model carbon that is used in this work (Figures 2b, S7).\(^{[13,14]}\)

![Scheme 2. Approach to the in situ DRIFT investigation of the carbon surface oxide ensemble in oxidizing atmosphere.](image-url)
Figure 2. [a] Typical in situ DRIFTS experiment monitoring the surface oxidation of R-AMC at 200 °C over 900 min (25 mg R-AMC, 6 vol-% O₂, 50 mL min⁻¹ (STP) total volume flow, inert gas He). [b] Mathematical deconvolution of the carbonyl band with gaussian functions. [c] Time resolved carbonyl band integral of carboxylic anhydrides (anhydrides I), at various temperatures (25 mg R-AMC, 6 vol-% O₂, 50 mL min⁻¹ (STP) total volume flow, inert gas He). Solid lines are guides for the eye.

It should be noted that the proposed DRIFTS approach can only provide a semiquantitative analysis, that enables the time resolved monitoring of the relative concentration of a given species (Figure 2c). The time resolved monitoring of the intensity of the anhydride contribution can subsequently be utilized to evaluate if the surface oxide ensemble reaches an equilibrium composition over the course of 1000 min TOS. Comparison of the development of the relative anhydride concentration at different temperatures shows that a true steady state is only achieved within 1000 min TOS at temperatures > 200 °C, since at lower temperatures the band integral is still slowly increasing. However, since the change in surface composition at the end of all experiments appears to be sufficiently small, the average of the last three spectra of each experiment (corresponding to an average time on stream of 900 min) was used to compare the surface oxide ensembles at different temperatures and atmospheres (Figure 3a–c). As expected, in an oxygen containing atmosphere, the total integral of the carbonyl band after 900 min TOS, that resembles the degree of oxidation of R-AMC, initially increases sharply with increasing temperature, and reaches a maximum at 220 °C (Figure 3a, for contour plots of all measurements, see Figure S8). At temperatures exceeding 220 °C, the integral of the carbonyl band after 900 min TOS decreases, which can be attributed to the starting decarbonylation of carboxylic acid groups. This sharp decline appears to be also a consequence of the formation pathway of anhydrides and lactones, that might proceed via the condensation of neighboring carboxylic acids and carboxylic acids and hydroxyl groups, whereas a lower concentration of carboxylic acids due to an increasing desorption rate lowers simultaneously the overall concentration of lactones and anhydrides. A similar behavior is observed for the oxidation of R-AMC with O₂ in the presence of H₂O, with the total integral increasing significantly with rising temperature, passing through a maximum at 220 °C and a subsequent decrease with further rising temperatures (Figure 3b, S9). This trend is somewhat different when R-AMC is exposed to an atmosphere containing O₂ and MeOH, since the overall integral does not pass through a maximum until 240 °C, before decreasing again at further elevated temperatures (Figure 3c, S10).

The composition of the surface oxide ensemble of R-AMC exposed to O₂ changes steadily with increasing oxidation temperature (Figure 3a). The proportion of anhydrides in the total carbonyl band integral increases (from 37 % at 140 °C to 72 % at 260 °C (anhydride I – II)), while the proportion of carboxylic acids decreases steadily (from 20 % at 140 °C to 7 % at 260 °C) as a consequence of increasing influence of thermal decarbonylation. Similar trends are also observed for the materials exposed to O₂/H₂O or O₂/MeOH, as the proportion of anhydrides increases for O₂/H₂O from 28 % at 140 °C to 61 % at 260 °C (Figure 3b) and for O₂/MeOH from 21 % at 140 °C to 52 % at 260 °C (Figure 3c). Simultaneously, the fraction of carboxylic acids decreases, for R-AMC exposed to O₂/H₂O from 21 % at 140 °C to 7 % at 260 °C and for R-AMC exposed to O₂/MeOH from 22 % at 140 °C to 13 % at 260 °C. Overall, the presence of H₂O or MeOH influences the anhydride concentration significantly, as it ranges 10 % (O₂/H₂O) to 20 percentage points (O₂/MeOH) below that determined for exposure to O₂ alone over the entire temperature range. This observation might be attributed to a shifted equilibrium of the condensation reaction of carboxylic acids, which is shifted to the reactants by the presence of water in the reaction atmosphere. Moreover, both water and MeOH could act as nucleophiles in the temperature range considered, inducing the opening of strongly electrophilic anhydrides in a hydrolysis/methanolysis reaction, with MeOH appearing to exert a greater influence in this respect compared to water. In all cases, the proportion of lactones remained largely constant over the entire temperature range while the decline in the integral fraction of carbonyl groups that is also observed in all atmospheres may be attributed to the tendency to form surface groups of higher state of oxidation with increasing temperature.
To verify the results of in situ DRIFT spectroscopy, the samples obtained by oxidation in the different atmospheres at 260 °C as well as the starting material R-AMC were further characterized by Boehm titration, TPD and XPS. As expected, Boehm titration shows a significant increase in acidity when R-AMC is exposed to oxidizing atmospheres at 260 °C, with the overall amount increasing by 129 %, from 1.12 mmol g⁻¹ for R-AMC to 2.58 mmol g⁻¹ in the presence of O₂ (Figure 3d). The sample oxidized with O₂ alone shows the highest overall acidity, with the total amount of acidic groups declining when H₂O (−6% from 2.58 mmol g⁻¹ for O₂–260 °C) or MeOH (−12% from 2.58 mmol g⁻¹ for O₂–MeOH–260 °C) is present. In the context of the high reaction temperature and the associated decarboxylation of carboxylic acids detected by DRIFTS, the surface acidity detected by Boehm titration can be ascribed to the presence of anhydrides, lactones and phenolic hydroxyl groups. Since the concentration of surface groups exhibiting higher pKₐ values (lactones, hydroxyl groups), as indicated by the consumption of Na₂CO₃ and NaOH, remains largely unchanged, it appears highly probable that the decline in the total amount of acidic groups in presence of H₂O and MeOH can be assigned to a loss of carboxylic anhydrides.

The desorption of carboxylic acid groups in the samples oxidized at 260 °C in different atmospheres is also confirmed by TPD, whereas only low amounts of carboxylic acids are determined by deconvolution of the CO₂ emission profiles (200–400 μmol g⁻¹) (Figures S11–S13). However, a decline in the overall concentration of acidic groups (carboxylic acids, anhydrides, lactones, phenols) cannot be unambiguously confirmed by TPD. In comparison to the samples oxidized in presence of O₂ and H₂O, TPD of the sample oxidized with a co-feed of O₂ and MeOH reveals a significant emission peak located at 380 °C of a species with a relative mass of m/z 31 (corresponding to CH₃O⁺), that represents strong evidence for the desorption of chemisorbed MeOH (Figure 3e). Considering the hypothesis that anhydrides might be prone to nucleophilic attack by MeOH, the emission of CH₃O⁺ can be assigned to the decomposition of methyl esters, that are the reaction product of the methanolyis of anhydrides (as well as the trans-esterification of lactones, and the esterification of carboxylic acids). The temperature range of the CH₃O⁺...
emission fits well to the decomposition temperature of non-cyclic esters on carbon surfaces reported in the literature.\(^{[13]}\)

XPS analysis of the samples oxidized at 260 °C in various atmospheres does not yield any obvious trends, likely due to the difficulties of XPS in distinguishing carboxylic acid derivate (Figures S14–S17 and Tables S1–S2). However, both analysis of the C1s and O1s spectra showed that the sample oxidized in presence of MeOH exhibits the highest concentration of carbon bound to oxygen by a single bond and oxygen species bound to carbon by single bonds, respectively, hinting at the chemisorption of MeOH which was also detected by TPD.

To further clarify the impact of \(\text{H}_2\text{O}\) and MeOH on the composition of the carbon surface oxide ensemble, \textit{in situ} DRIFTS experiments in absence of \(\text{O}_2\) were carried out. For these measurements, R-AMC oxidized at 260 °C for 900 min in presence of 6 vol-% \(\text{O}_2\) served as starting material (designated as R--AMC--O\(_2\)--260 °C, Scheme 3).

The exposure of R--AMC--O\(_2\)--260 °C to a temperature of 260 °C in an inert gas flow did not show any significant changes in the carbonyl absorption range (Figures 4a, S18a). However, exposure to 1.5 vol-% \(\text{H}_2\text{O}\) at 260 °C for 900 min TOS resulted in a significant decrease of absorption in the carbonyl range, with the absorption minimum being centered around 1800 cm\(^{-1}\) and a shoulder positioned at 1850 cm\(^{-1}\) (Figures 4b, S18b). The observed absorption minima correlate directly with the carbonyl absorption maxima of carboxylic anhydrides at 1792 cm\(^{-1}\) and 1852 cm\(^{-1}\), indicating that carboxylic anhydrides are hydrolyzed in presence of water vapor at 260 °C. Simultaneously, a build-up of carboxylic acids as hydrolysis products cannot be observed (absorption maximum at 1758 cm\(^{-1}\)), indicating a quick decarboxylation at 260 °C. A similar, but even faster decrease in absorption with minima centered at 1795 cm\(^{-1}\) and 1850 cm\(^{-1}\) could be observed in presence of 1.5 vol-% MeOH at 260 °C, underscoring the

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**Figure 4.** \textit{In situ} DRIFTS experiments, R-AMC oxidized at 260 °C in 6 vol-% \(\text{O}_2\) for 900 min as starting material is exposed to [a] He at 260 °C; [b] 1.5 vol-% \(\text{H}_2\text{O}\) in He at 260 °C and [c] 1.5 vol-% MeOH in He at 260 °C (25 mg R-AMC--O\(_2\)--260 °C, 50 mlmin\(^{-1}\) (STP) total volume flow). The insets depict the DRIFT spectra after 900 min TOS in the range between 1625 and 1875 cm\(^{-1}\). [d] Boehm titration of R--AMC--O\(_2\)--260 °C and the materials exposed to He, \(\text{H}_2\text{O}\) and MeOH at 260 °C for 900 min. [e] Concentration of surface oxides derived from by deconvolution of the TPD CO\(_2\) emission profile of R--AMC--O\(_2\)--260 °C and the materials exposed to He, \(\text{H}_2\text{O}\) and MeOH at 260 °C for 900 min.
lability of carboxylic anhydrides towards nucleophilic attack (Figures 4c, S18c). In presence of MeOH the loss of absorption appears also to be partly caused by methanolysis of lactones, which exhibit an absorption maximum at 1771 cm\(^{-1}\), as the negative absorption band additionally shows a shoulder centered at 1775 cm\(^{-1}\). Below 1700 cm\(^{-1}\) a further loss in absorption can be observed in the range between 1625 cm\(^{-1}\) to 1675 cm\(^{-1}\). However, since substituted C=C double bonds, certain carbonyl (e.g. quinones) and carboxylate species are known to contribute to this spectral region, an exact assignment cannot be made.\(^{[17]}\) It should be noted at this point, that no significant increase or decrease in absorption in the 3000 to 4000 cm\(^{-1}\) spectral region could be observed, indicating that the concentration of hydroxyl groups is not influenced by the presence of H\(_2\)O or MeOH (Figure S18).

Characterization after the in situ DRIFTS experiments was conducted by Boehm titration, TPD and XPS. Boehm titration supports the interpretation of DRIFTS, the total amount of acidic species decreases when R–AMC–O\(_2\)-260 °C is contacted with H\(_2\)O (−5 %, from 2.58 to 2.45 mmol g\(^{-1}\)) or MeOH (−12 %, from 2.58 to 2.26 mmol g\(^{-1}\)) at 260 °C (Figure 4d). This applies in particular to the oxidized amorphous carbon treated with MeOH, whereas the decline in the total amount of acidic groups can be predominantly assigned to a significant decrease of the amount of highly acidic species, indicated by a drop of 19% in NaHCO\(_3\) consumption and of 33% in Na\(_2\)CO\(_3\) consumption compared to R–AMC–O\(_2\)-260 °C. This decrease in acidity can be mainly assigned to consecutive reactions taking place after anhydride cleavage, with the decarboxylation of the initially formed carboxylic acids being responsible for the drop in overall acidity. Simultaneously, the presence of H\(_2\)O or MeOH in the reaction atmosphere does not appear to exert any significant influence on acidic groups of high pK\(_a\) (phenolic hydroxyl groups), as indicated by an unchanged consumption of NaOH. The finding that carboxylic anhydrides are labile to nucleophilic attack by H\(_2\)O and MeOH is further supported by the deconvolution of the TPD CO\(_2\) emission profiles, which show a drop in anhydride concentration of 16 % for the H\(_2\)O treated sample and of 20 % for the sample exposed to MeOH compared to the starting material R–AMC–O\(_2\)-260 °C (Figure 4e, Figures S19–21). In case of the oxidized carbon exposed to MeOH at 260 °C, the lactone concentration also drops by 14 %. Analysis of the XPS C1s contribution shows a reduction in the surface concentration of carboxylic acid derivates of the carbons treated with H\(_2\)O (−5 %) and MeOH (−12 %), that matches the decrease in overall acidity determined by Boehm titration (Figures S22–S24, Tables S1–S2). However, it is conceivable that the error of the XPS analysis is situated in the range of ±5 %, so that these results must be treated with caution. Similarly, the decrease in surface concentration of C=O species in the XPS O1s spectrum of R–AMC–O\(_2\)-260 °C upon exposure to MeOH can be observed even without deconvolution, as a comparison of the normalized O1s contributions shows a clearly visible decrease in signal intensity around 531 eV for the MeOH treated carbon (Figure S14). This decrease in carbonyl oxygen species can on one hand be assigned to the reduction of carbonyl groups (ketones, quinones), and on the other hand to the cleavage of anhydrides and lactones and the consecutive decarboxylation of the resulting carboxylic acid groups.

Based on the results of the in situ DRIFTS experiments and post mortem characterization, a mechanism of high temperature DME formation on oxidized carbon materials can be developed, that is able to explain the catalytic behavior observed in context of MeOH conversion over O-PDC (Scheme 4). At a temperature of 300 °C, only a small amount of carboxylic acid groups is present on the catalyst surface, due to the fast decarboxylation reaction that exhibits an onset around 240 °C. However, carboxylic anhydrides and lactones are thermally stable at 300 °C, with the well-known onsets for anhydride desorption at 400 °C and of lactone decomposition at 600 °C.\(^{[16,19]}\) In case of MeOH conversion over carbon, these

![Scheme 4. Equilibria of surface oxide species and DME formation pathway during MeOH conversion at 300 °C over carbon catalysts.](image)
species act as thermally stable, acidic “reservoir”, as nucleophilic constituents of the reaction atmosphere such as MeOH and H₂O are able to activate anhydrides and lactones by methanolysis and hydrolysis, respectively. In situ DRIFTS and post mortem characterization results suggest that carboxylic anhydrides represent the electrophile of higher reactivity compared to lactones. Hydrolysis of carboxylic anhydrides and lactones yields carboxylic acids, which are short-lived under reaction conditions and prone to decarboxylation. However, nucleophilic cleavage of anhydrides and lactones with MeOH appears to proceed faster than the corresponding reaction with H₂O, and yields a methyl ester, which appears to be a key intermediate in DME formation. Our hypothesis on DME formation involves a second MeOH molecule, which is activated by a hydrogen bond to the carbonyl oxygen, that attacks the methyl group of the ester under proton transfer to the carbonyl oxygen. DME desorption yields a carboxylic acid, however, disrupts the catalytic cycle, which involves a second MeOH molecule, which is activated by a hydrogen bond to the carbonyl oxygen, that attacks the methyl group of the ester under proton transfer to the carbonyl oxygen. DME desorption yields a carboxylic acid, however, disrupts the catalytic cycle, which can subsequently only be restarted in presence of O₂ by reoxidation of the carbon matrix. It should be noted that another temperature stable, acidic surface group present on the carbon catalysts are hydroxyl groups. However, Boehm titration of spent samples (Figures 3d and 4d) did not yield any evidence of an interaction between hydroxyl or carboxyl groups (under elimination of H₂O), regenerating the initial anhydride or lactone. Decarboxylation of the formed carboxylic acid, however, disrupts the catalytic cycle, which can subsequently only be restarted in presence of O₂ by reoxidation of the carbon matrix. The catalytic activity of the catalyst slowly declines in absence of O₂, as nucleophilic cleavage of anhydrides as well as DME formation yields carboxylic acid groups, whereas decarboxylation competes with re-condensation to anhydrides and lactones and leads to a slow decline of the surface concentration of carboxylic acid derivatives as catalytically active sites. Since carboxylic anhydrides and lactones as acidic reservoir species are thermally quite stable, heat treatment at 500°C in inert atmosphere does not lead to a noticeable decline in acid/base catalytic activity, the renewed formation of (in comparison to anhydrides and lactones) thermally labile intermediates such as the methyl ester (desorption maximum close to 400°C) appears to be fast. However, heat treatment at 500°C in presence of MeOH leads to the nucleophilic cleavage of anhydrides and lactones yielding thermally less stable carboxylic acids and methyl esters that are prone to thermal decomposition. Due to this reaction sequence, most carboxylic acid derivates are degraded, and only a slow regeneration of acid/base catalytic activity can be observed upon reintroduction of oxygen.

Conclusion

In a combined approach, MeOH conversion over a graphic polymer-derived carbon was studied and correlated with in situ DRIFT spectroscopy, performed on a closely related amorphous polymer-derived carbon, and with extensive post mortem characterization of the carbon surface oxide ensemble. In this context, we could show that oxidized carbon materials can act as highly active high-temperature solid acid catalysts in the dehydration of MeOH, with selectivity to DME at 300 °C of up to 92% at a conversion of 47%. The high-temperature acidity of oxidized carbons could be attributed to the interaction of thermally stable carboxylic anhydrides and lactones and nucleophilic constituents of the reaction atmosphere, i.e. MeOH and H₂O. The reaction of MeOH with carboxylic acid derivates leads to the formation of a methyl ester, which was identified as key intermediate of DME formation on oxidized carbon catalysts. Elucidation of the mechanism of this substrate induced acidity can now serve as the starting point for the targeted design of a new generation of low cost, metal-free, carbon-based solid acid catalysts with specific surface functionalization. In this context, the scope of applications for these novel solid acid catalysts may be extended to etherification, esterification or dehydration of higher alcohols beyond MeOH, in order to obtain technically attractive ethers, esters and olefins.

Finally, the demonstrated strategy for enabling in situ DRIFTS analysis of carbon surface species promises new insights and a deeper understanding of the dynamics of carbon surface species under reaction conditions in a wide range of applications such as energy storage and conversion as well as heterogeneous catalysis.

Experimental Section

Materials. All gases were purchased from Westfalen AG. Phloroglucinol, chloroacetic acid and HPLC-grade methanol were purchased from Acros Organics, Pluronic F127, 37 wt-% formaldehyde solution and lithium aluminum hydride were supplied by Sigma Aldrich. From Fisher Scientific, 37 wt-% hydrochloric acid, sodium hydroxide, potassium iodide, technical grade ethanol, HPLC-grade tetrahydrofuran, and 65 wt-% nitric acid were acquired. Nickel(II) chloride hexahydrate was acquired from Alfa Aesar. Standard solutions for Boehm titration (0.01 M HCl, 0.01 M KOH, 0.01 N Na₂CO₃, 0.01 N NaHCO₃) were purchased from Merck.

Preparation of the precursor polymer. To obtain the carbon precursor, a synthesis procedure following Chai et al. was applied. In short, in a 3 L round bottom flask, 26.2 g Phloroglucinol (1,3,5-trihydroxy benzene), 52.4 g Pluronic® F127 and 10 g 37 wt-% HCl are heated under stirring with a KPG stirrer (500 rpm, half-moon...
impeller, 70 mm blade) in 1320 mL EtOH to reflux. Upon addition of 26 g 37 wt-% aqueous formaldehyde solution, the reaction mixture turns white in minutes. After refluxing for 2 h, a yellow precipitate is collected by filtration. After washing thoroughly with EtOH and vacuum drying at 30 mbar and 60 °C, 47.3 g of bright yellow polymer aggregates are obtained.

Preparation of the graphitic polymer-derived carbon (PDC). The graphitic polymer derived carbon (PDC) is prepared according to a procedure established by Herold et al.[10] 45 g of the precursor polymer and 4.2 g potassium iodide are suspended in 1300 ml EtOH. Under stirring with a KPG stirrer, 75 g NaOH in 400 mL H₂O are slowly added to the reaction mixture. Over the course of 1 h, a mixture of 75 g of chloroacetic acid and 31 g NaOH in 250 mL H₂O is added dropwise under stirring to the reaction suspension. After stirring for additional 23 h at room temperature, the polymer particles are collected by filtration and washed thoroughly with EtOH and H₂O. By drying at 30 mbar and 60 °C, 44 g of red-brown polymer aggregates are obtained. Initially, in order to load the carbonyl functionalized polymer with H⁺-ions, 40 g of the polymer particles are suspended in 500 mL 10 wt-% HCl for 30 min on an orbital shaker. Subsequently, the red polymer aggregates are filtrated, washed with deionized H₂O, and suspended again in 500 mL of a 1 M solution of nickel(II) chloride hexahydrate in EtOH. Under stirring with a KPG stirrer, 75 g NaOH in 400 mL H₂O is added until the precipitate (Al(OH)_3) is completely dissolved. The mixture is added dropwise to the reaction suspension. After 1 h, the suspension is cooled to 0 °C, and the reaction mixture is heated to reflux. Subsequently, after 24 h and once more after 48 h, 3 g fresh LiAlH₄ are added. After 72 h, the suspension is cooled to 0 °C, and the reaction is quenched with vigorous stirring by dropwise addition of isopropanol and water. When the gas evolution upon addition of H₂O has stopped, 37 wt-% HCl is added until the precipitate (Al(OH)_3) and LiOH which formed upon LiAlH₄ neutralization is completely dissolved. The carbon is collected by centrifugation and is initially washed with a mixture of 5 wt-% HCl and MeOH (70:30 vol-%), and subsequently with a mixture of deionized H₂O and MeOH (70:30 vol-%). After drying overnight at 60 °C and 30 mbar, 1.05 g of reduced amorphous model carbon (R-AMC) are obtained.

**Catalytic testing.** Catalytic reactions were performed in a continuous flow apparatus with a quartz tube as reactor featuring an internal diameter of 4 mm in which the catalyst (~100 mg) was placed between two glass wool plugs. Methanol was fed to the reactor via a two-stage saturator system, gas dosing was realized by mass flow controllers. Typical experiments were conducted at 300 °C, while 1.5 vol-% MeOH, 8 vol-% O₂ at 20 mL min⁻¹ (STP) total volume flow with He as inert gas were used. Heating and cooling was conducted with a fixed rate of 5 °C min⁻¹. Off-gas analysis was simultaneously performed by online mass spectrometry (QAMS, InProcess Instruments) and by an online gas chromatograph equipped with thermal conductivity and flame ionization detector (GC2010 plus, Shimadzu).

**In situ DRIFT spectroscopy.** In situ DRIFTS experiments were carried out in a VERTEX 70 spectrometer (Bruker) employing a Praying Mantis diffuse reflection accessory (Harrick Scientific) in combination with a propriety measurement-cell,[23] in which the reaction gas flows through the sample during DRIFTS experiments. Employing an N₂-cooled MCT detector and an aperture of 3.5 mm, spectra were usually recorded every 1200 s by averaging 300 scans at a resolution of 1 cm⁻¹. In a typical measurement, 25 mg of carbon were studied in an atmosphere containing 1.5 vol-% MeOH or H₂O (supplied by two-stage saturators) with or without addition of 6 vol-% O₂ with He as inert gas at a total volume flow of 5 mL min⁻¹ (STP). The sample is heated to the desired temperature in an atmosphere containing He and MeOH or H₂O if required, the reference spectrum is recorded, and the measurement is started by simultaneously starting the recording of spectra and switching on the oxygen feed (if O₂ is required).

**In situ DRIFT spectra presented in waterfall plots and contour plots were subjected to a 1-point baseline correction because the baseline shifts during the measurement due to the slow heating of the liquid N₂ cooled MCT detector. For the baseline correction, the absorption in the spectral region between 2025 cm⁻¹ and 1975 cm⁻¹ was averaged and subtracted from the spectrum. In addition to the baseline correction, the spectra were smoothed over 10 points using the moving average method. For the mathematical evaluation of the carbonyl band, the raw data was used as a starting point. In this case, a 2-point baseline correction was performed by averaging the spectral regions between 1700 cm⁻¹ and 1690 cm⁻¹ and between 1885 cm⁻¹ and 1875 cm⁻¹ and using them as grid points for a linear regression. The determined linear function was then subtracted from the spectrum as a baseline for the carbonyl band between 1700 cm⁻¹ and 1875 cm⁻¹. Subsequently, the carbonyl band was fitted with five Gaussian profiles following a least squares method. The solver plugin of Microsoft Excel 2016 was used for this purpose, using the Evolutionary Algorithm. For the fitting, the maximum of the...
contribution of carbonyl groups was fixed between 1739 and 1746 cm\(^{-1}\), the maximum of carboxylic acids between 1760 and 1776 cm\(^{-1}\), that of lactones between 1773 and 1776 cm\(^{-1}\), that of anhydrides I between 1790 and 1795 cm\(^{-1}\), and that of anhydrides II between 1835 and 1850 cm\(^{-1}\). The full width at half maximum was constrained between 35 and 40 cm\(^{-1}\) for each species except for the absorption maximum of anhydrides II, where it was fixed between 35 and 50 cm\(^{-1}\) to obtain a better fit.

**Analytics.** Temperature programmed desorption was conducted in a STA 409PC Luxx thermogravimetry device (NETZSCH GmbH) coupled to an online mass spectrometer (Omnistar, Pfeiffer Vacuum GmbH). Under a stream of 3 cm\(^3\) min\(^{-1}\) (STP) He, 50 mg of a carbon sample were initially heated with a rate of 5 °C min\(^{-1}\) to 100 °C, allowing the sample to dry for 2 h. Subsequently, the sample was heated from 100 °C to 1000 °C with a rate of 5 °C min\(^{-1}\). The mass spectrometer was calibrated utilizing (gravimetrically) premixed gas mixtures (Westfalen AG, 2 vol-% CO\(_2\) in He, 2 vol-% CO\(_2\) in He, 5 vol-% O\(_2\) in He and 2% N\(_2\) in He). H\(_2\)O was calibrated by feeding a defined amount of O\(_2\) (prior calibrated by a defined gas mixture) and H\(_2\) to a total oxidation catalyst (Pt/Al\(_2\)O\(_3\), Shimadzu Corp.) at 350 °C. The analytical error, determined by the combined thermogravimetric/TPD analysis of a known amount of CaC\(_2\), was found to be around 5%. Deconvolution of the TPD profiles was carried out building on work on parts of Pereira, Figueredo and co-workers by utilizing Gaussian functions and a least squares fit procedure.[15] In case of the CO\(_2\) emission profile, the temperature maximum of carboxylic acids was positioned at 310 ± 25 °C, that of anhydrides at 500 ± 50 °C and that of lactones at 675 ± 50 °C. In a similar manner, deconvolution of the CO emission profiles was carried out assuming the position of the desorption maxima of primary alcohols at 410 ± 50 °C,[16] of phenols at 535 ± 50 °C[17] of carbonyl groups (aldehydes, ketones) and ethers at 700 ± 50 °C and of quinones at 900 ± 100 °C.

The full width at half maximum (HWHM) was fixed for all contributions to a range of 100 ± 50 °C. Boehm titration was carried out following a procedure proposed by Ackermann et al.[18] In short, 50 mg of a carbon sample are dispersed for 72 h under inert atmosphere in 40 mL of 0.01 N NaHCO\(_3\), Na\(_2\)CO\(_3\), and NaOH. After carbon removal by filtration, 10 ml aliquots of the base solutions are mixed with 15 mL of 0.01 N HCl each, and are subsequently titrated with a 0.1 N Na\(_2\)CO\(_3\) solution using an automatic potentiometric titrator (Mettler Toledo T50). All results of Boehm titration are corrected by a corresponding blank measurement. The error ranges shown are the standard deviations of the final titration of aliquots of the base solutions that came in contact with the samples. X-ray photoelectron spectroscopy was performed on a Quantera II XSM (Physical Electronics) using monochromatic Al K\(_\alpha\) irradiation (1486.6 eV) operating the anode at 15 kV with a spot diameter of 200 μm. The energy axis was calibrated by fixing the C1s contribution of sp\(^2\) carbon (“graphite”) at 284.6 eV. For deconvolution, linear combinations of Gaussian and Lorentzian functions were utilized (“pseudo-Voigt”-profiles) and Shirley background subtraction was performed prior fitting. Deconvolution of the C1s and O1s regions was performed according to Kundu et al., assuming the contribution of non-functionalized sp\(^2\)-carbon at 284.6 ± 0.1 eV, carbon bound to oxygen by a single bond at 286.1 ± 0.1 eV, carbon bound to oxygen by a double bond at 287.5 ± 0.1 eV, carboxylic acid derivatives at 288.7 ± 0.1 eV and the π − π* transition satellite at 290.5 ± 0.1 eV.[19] The full width at half maximum (FWHM) was restricted to values between 1.4 and 1.6 eV. Shape factors (ratio of Lorentzian/Gaussian functions) were kept equal for all functions during the fit, and were usually located close to 0.5.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** acid/base catalysis · carbon materials · carbon surface chemistry · heterogeneous catalysis · in situ spectroscopy

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