Raman Spectroscopic Characterization of Environmentally Friendly Binder Systems for Carbon-Bonded Filters

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A contribution to the production of zero-defect materials is the development of carbon-bonded alumina foam filters for removing nonmetallic inclusions from molten metals. Herein, such filters containing various mixtures of Carbores P, lactose, and tannin as binder are investigated by Raman spectroscopy. The filter samples differ in whether or not they are fired and whether or not n-Si is added to them. Raman measurements are also performed on samples of the individual binder substances, which have been preannealed at temperatures up to 1400 °C. The variation of the sp² carbon cluster sizes due to the heat treatment is estimated using the intensity ratio of the D and G bands as determined from these measurements. The conversion of the samples from hydrogen-rich amorphous carbon systems to nanocrystalline graphite is observed. The results show no significant differences between the binders in regard to the material properties that can be studied with Raman spectroscopy.

1. Introduction

To improve the mechanical properties of steel products, e.g., their fracture toughness, tensile strength, ductility, and fatigue resistance, it is crucial to reduce the amount of nonmetallic inclusions in the steel melt during the production process. An efficient way to do so is the use of ceramic foam filters, which are typically made using raw materials such as silicon carbide or zirconia.[1,2] Another example is carbon-bonded alumina filters, which have the advantage of excellent high-temperature properties such as high corrosion resistance and thermal shock endurance.[1] The alumina filters are typically produced in an open-cell foam structure according to the Schwartzwalder technique,[4] which means that polyurethane foams are impregnated and sprayed in different steps with a slip. Frequently, substances from the group of synthetic resins, pitch-bonded systems, or bitumens are used as binders. Unfortunately, all of them contain the carcinogenic benzo[a]pyrene. Within the collaborative research center 920 (CRC 920) “Multi-Functional Filters for Metal Melt Filtration – A Contribution towards Zero Defect Materials” at TU Bergakademie Freiberg solutions to this issue are investigated. A promising approach is the use of alternative binders such as Carbores P,[5,6] which has been shown to yield drastically less benzo[a]pyrene. To completely avoid benzo[a]pyrene, a combination of tannin and lactose for the binder was studied.[7,8] However, pure lactose/tannin filters were shown to possess a lower carbon yield and mechanical properties that are not entirely satisfactory, mainly in the form of a low cold crushing strength.[8] To improve the carbon yield of these alternative binder systems, the addition of n-Si has been suggested.[5,6] To obtain filters with both the desired properties and a small benzo[a]pyrene footprint, binder systems based on a mixture of Carbores P, lactose, and tannin were studied in this article.

The aim of this work is to investigate the influence of the binders Carbores P, tannin, and lactose as well as the additive n-Si on the chemical structure of the filters using Raman spectroscopy, testing binder compositions that have not been covered by other studies yet. Furthermore, the effect of thermal treatment on the samples is examined. Thus, this article follows in the footsteps of previous publications that have demonstrated the merits of Raman spectroscopic studies on carbon-bonded filter materials[6,8,11,12] and complements these.

Raman spectroscopy is a widely used method to investigate carbon systems because it is nondestructive, fast, and has a high lateral resolution. The basis of Raman spectroscopy is the Raman effect, which describes the inelastic scattering of light on matter. During inelastic scattering, a phonon is either created (Stokes scattering) or annihilated (anti-Stokes scattering), which causes an energy difference between the scattered and the incident light. This energy difference is measured and displayed on the x-axis of Raman spectra in units of a wavenumber, whereas the y-axis shows the intensity of the respective scattered light. The position, intensity, and shape of Raman peaks provide information on
vibrations within the sample, which can be used as a fingerprint for substance identification\cite{11} or for determining chemical and physical properties. In the context of carbon-containing systems, these properties include the $sp^2$ carbon cluster sizes, the degree of bond disorder, and the $sp^2/sp^3$ ratio.\cite{14}

2. Experimental Section

2.1. Sample Preparation

Two types of samples were investigated, namely, carbon-bonded alumina filters produced from slip on one hand and the raw materials Carbores P, tannin, and lactose on the other hand.

2.1.1. Fabrication of Carbores P, Lactose, Tannin Samples

The samples of the raw materials Carbores P, lactose, and tannin were manufactured as follows. The powders of the three substances were separately filled into sealed alumina crucibles. TiO$_2$ was added to the lactose powder to prevent foaming. Each of the binders was put in a crucible, placed in a steel retort, and embedded in petroleum coke, ensuring a reducing atmosphere. Subsequently, the binder materials were pyrolized for 180 min at 100, 200, 400, 600, 800, 1000, 1200, and 1400 °C, respectively. The heating was performed at 1 K min$^{-1}$ and the cooling at 3 K min$^{-1}$ to avoid damage to the alumina crucibles.

2.1.2. Fabrication of Carbon-Bonded Alumina Samples

In total, four series of carbon-bonded alumina samples called A, B, C, and D were manufactured. Each sample series consisted of six samples with varying percentages of lactose, tannin, and Carbores P. The series differed in whether or not n-Si was added and whether or not the samples were pyrolized (see Table 1).

All samples were obtained from dried slips, whose composition is shown in Table 2, along with the corresponding manufacturers. The largest part of the raw materials consisted of aluminum oxide, whereas Carbores P, lactose, and tannin were used as both binders and carbon sources. The total mass fraction of the binders was always 20 wt%. In the header of Table 2, the sp$^2$/sp$^3$ ratios of the respective Carbores P to lactose/tannin ratios.

In the sample series B and D, n-doped silicon was added to increase the carbon yield.\cite{9} The amount of added silicon was chosen to be equal to 5 wt% of the lactose/tannin content in the respective sample.

The first step of filter production consisted of mixing all solid components as powders. The liquid additives were mixed with deionized water, which was then added to the powder mix. The total solid content added up to 78%.

For this work, the slip was air dried until it became a hard paste. This paste was pestled and pressed into tablets. The tablets for the sample series A and B were not treated further, while the C and D samples were heated according to the step-wise heat treatment described in Emmel and Aneziris.\cite{15} For this, the samples were placed in a retort embedded in petroleum coke. The heat treatment was performed at a heating rate of 1 K min$^{-1}$ and with 30 min dwell time after every 100 °C until a

| Table 1. Difference in treatment of the four sample series A, B, C, and D for the carbon-bonded alumina samples that were investigated in this study. |
|---|---|---|---|
| | A | B | C | D |
| n-Si | – | x | – | x |
| Fired | – | – | x | x |

| Table 2. Slip composition. Each sample series consists of six samples, which differed in their Carbores P to lactose/tannin ratios. The sample names in the table header represent these ratios. |
|---|---|---|---|---|---|---|
| | Raw materials | Additives | Related to the total of raw materials (in wt%) | Related to lactose/tannin (in wt%) | Total solid content (in wt%) | Slip |
| | 100/0 | 80/20 | 40/60 | 60/40 | 20/80 | 0/100 | |
| **Raw materials** | | | | | | | 78.0 |
| Martoxid MR70 \cite{4} | 66.0 | 66.0 | 66.0 | 66.0 | 66.0 | 66.0 | |
| Carbores P \cite{5} | 20.0 | 16.0 | 12.0 | 8.0 | 4.0 | 0.0 | |
| Lactose \cite{6} | 0.0 | 3.3 | 6.7 | 10.0 | 13.3 | 16.7 | |
| Tannin \cite{7} | 0.0 | 0.7 | 1.3 | 2.0 | 2.7 | 3.3 | |
| Carbon black N 991 \cite{8} | 6.3 | 6.3 | 6.3 | 6.3 | 6.3 | 6.3 | |
| Graphite AF 96/97 \cite{9} | 7.7 | 7.7 | 7.7 | 7.7 | 7.7 | 7.7 |
| **Additives** | TiO$_2$ \cite{10} | 0.0 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | Al \cite{11} | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| | SiO$_2$ \cite{12} | 0.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| Castament VP 95 L \cite{13} | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Contraspum K 1012 \cite{14} | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Ammonium ligninsulfonate \cite{15} | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| n-Si \cite{16}, \cite{17} | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |

\cite{4}Martinswerk, Germany; 99.80 wt% Al$_2$O$_3$, d$_{44} < 3.0$ μm; \cite{5}Rütgers, Germany; \cite{6}l-lactose monohydrate DAB 9, DM-Markt, Germany; \cite{7}Quebracho extract, type Indusol ATO, Otto Dille, Germany; \cite{8}Luvomaxx N-991, Lehmann & Voss & Co., Germany, ≥ 99.0 wt% carbon, > 0.01 wt% ash content, primary particle size: 200–500 nm; \cite{9}AF 96/97, Graphit Kropfmühl, Germany, 96.7 wt% carbon, 99.8 wt% < 40 μm; \cite{10}Nanopowder TR, ≥ 99.9 wt% rutile, Crenoex GmbH, Germany; \cite{11}Al-Grießflocke 0–75 μm, ≥ 99.6% Al, d$_{44} = 29.0$ μm, Hoech granules GmbH, Germany; \cite{12}R-W-Filler weiß RW silicium GmbH, Germany; \cite{13}BasF, Germany; \cite{14}Zschimmer & Schwarz, Germany; \cite{15}Otto Dille, Germany; \cite{16}Grade 1a, > 99.9% n-Si, particle size< 63 μm, Silchem, Germany; \cite{17}Only in sample series B and C.

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maximum temperature of 1000 °C was reached, at which the samples were held for 180 min.

2.2. Raman Spectroscopy

All measurements were performed at room temperature (RT) with a Raman spectrometer from Horiba Jobin Yvon (Labram HR 800). As excitation source, a frequency-doubled Nd:YAG laser (532 nm) was utilized. The laser light was focused on the sample surface with an Olympus objective with 50× magnification. An optical filter was used to reduce the laser power on the surface to 2.5 mW to avoid heating the samples. The measurements were performed in backscattering geometry, which means that the scattered light was collected by the same objective that was also used to focus the incident light.

The scattered light was diffracted into different wavelengths by a 600 mm grating and detected by a Peltier cooled CCD detector. Each spectrum was recorded with measurement times of 10 × 3 s or 10 × 6 s.

2.3. Density Functional Theory (DFT)

DFT calculations were performed on trans-decapentaene (trans-DP) and trans-dodecahexaene (trans-DDH), two finite-length approximations of trans-polyacetylene (trans-PA) with 10 and 12 carbon atoms, respectively. Trans-PA is a hydrocarbon which contains a chain of sp² carbon atoms with alternating single and double bonds between them; the repeating unit of this polymer is C₂H₂. The DFT calculations were performed in the local density approximation, using the exchange-correlation energy functional proposed by Perdew and Wang. All calculations were performed with the help of version 1.7.x of the PySCF electronic structure code, and the Perdew–Wang functional was accessed using a PySCF interface to version 4.3.4 of the Libxc library. Moreover, the valence triple-ζ basis set aug-cc-pVTZ was chosen in combination with a pruned numerical integration mesh of PySCF grid level 7. This grid level is equivalent to (90,974) atomic grids for the hydrogen atoms and (135,1202) atomic grids for the carbon atoms. Further, a self-consistent field energy convergence threshold of 10⁻⁸ E_h was applied, with E_h denoting the energy unit Hartree. With these calculation parameters, the initial nuclear geometries for trans-DP and trans-DDH were optimized using the FIRE algorithm until the atomic forces were below 10⁻⁸ E_h/\(a_0\); here, \(a_0\) represents the Bohr radius. The initial geometries were taken from the ChemSpider database, i.e., ChemSpider ID 4942094 for trans-DP and ChemSpider ID 29316890 for trans-DDH. On the optimized nuclear geometries, Raman spectra were calculated following the finite difference approach by Porezag and Pederson. Both the geometry optimization and the calculation of the Raman spectra were realized via an interface to the ASE software package.

2.4. Carbon Content Measurements

The total carbon concentration of the filter samples was determined by high-frequency induction combustion analysis using a CS744 (LECO, USA). The samples were ground so that the grain size was well below 100 μm and mixed with copper as an induction accelerator reagent. For each sample, three measurements were performed, and the mean value as well as the standard deviation were calculated.

3. Results and Discussion

3.1. Raman Spectra of Pure Carbores P, Lactose, Tannin Samples

3.1.1. Carbores P

The spectra of the Carbores P samples preannealed in a temperature range from room temperature (RT) up to 1400 °C are shown in Figure 1. The two main features in all spectra are the D peak around...
1360 cm\(^{-1}\) and the G peak around 1600 cm\(^{-1}\).\(^{[14,28,29]}\) While the G peak arises from in-plane stretching vibrations of \(sp^2\) carbon atoms, the D peak represents a breathing mode of aromatic rings, which exclusively occurs in the presence of disorder. Therefore, in highly ordered graphite, only the G peak can be measured.\(^{[28–30]}\)

From RT up to 600 °C, the D peak exhibits shoulders at 1170, 1240, and 1450 cm\(^{-1}\). Bands at these positions were assigned to trans-PA\(^{[31,32]}\), which prompted the DFT calculations mentioned in Section 2.3 in the first place. The observed bands are in very good agreement with the calculated Raman spectra for trans-DP and trans-DDH, which exhibit peaks around 1050, 1170–1190, 1220–1260, and 1560–1640 cm\(^{-1}\). In the experimental spectra, the peaks around 1600 cm\(^{-1}\) are overlaid by the G peak. The PA shoulders are largest at 600 °C. Even though these shoulders are very prominent in the spectra, the percentage of PA in the sample is probably low because PA has a large Raman cross-section.\(^{[31]}\)

Above 600 °C, the PA shoulders disappear, indicating that PA pyrolyzes in this temperature range. The large deviation of this finding from the decomposition temperature of 420 °C reported in the literature\(^{[33]}\) may be related to the differing external pressures. Specifically, the pyrolysis was studied in situ under vacuum in Ito et al.,\(^{[33]}\) whereas in this work, the samples were fired under a reducing atmosphere and analyzed afterward.

The spectra at room temperature show a high background, which originates from photoluminescence (PL) processes. In carbon samples, PL can occur due to a high hydrogen content.\(^{[34,35]}\) The mechanism of this PL is detailed in Robertson’s work.\(^{[36]}\) A rough estimation of the hydrogen mass fraction in the sample, \(H\,[\text{at}\%]\), is possible by evaluating the ratio of the slope of the PL background \(m\) and the intensity \(I_G\) of the G peak according to previous studies.\(^{[34,35]}\)

\[
H[\text{at}\%] = 21.7 + 16.6 \log\left(\frac{m}{I_G[\text{μm}]}\right) . \tag{1}
\]

To get the slope \(m\), the PL background was fitted in the range of 600–2300 cm\(^{-1}\). Although Equation (1) was proposed for a wavelength of 514 nm,\(^{[35]}\) the used wavelength of 532 nm is close enough for a first estimation. Evaluating Equation (1) for the Raman spectra of the samples preannealed at temperatures up to 400 °C results in a hydrogen content of about 40%. At 600 °C, the percentage of hydrogen decreases to 20–30%. From 800 °C upward, no significant slope of the PL background could be detected, which means the hydrogen content was well below 20%.\(^{[34,35]}\)

At higher wavenumbers in the region between 2500 and 3500 cm\(^{-1}\), broad bands with a maximum at 2950 cm\(^{-1}\) occur. These bands are a superposition of second order peaks from the D and G peaks and C–H vibrations.\(^{[35,37]}\) At even higher wavenumbers (around 3350 cm\(^{-1}\)), a broad band attributed to –OH vibrations can be seen. This band loses most of its intensity for temperatures above 400 °C, indicating that the OH groups have already split off.

For spectra at 800 °C and above, the Raman intensity decreases by a factor of 10 compared to the spectra at lower temperatures. To ensure that the shapes of the spectra were still recognizable, the intensities of all spectra were normalized with regard to the G peak. A reason for the drastic intensity loss could be a rapid decrease of the \(sp^2\) content in the samples at 800 °C. According to Ferrari et al.,\(^{[14]}\) this leads to a decrease in the optical gap or Tauc gap and, consequently, to an increase of absorption, which in turn results in a lower penetration depth of the laser light. Hence, as the penetration depth decreases, the excited volume decreases and thus the Raman intensity is lower.

With growing temperature, the position of the G peak as well as the intensity ratio of the D and G peaks increases, which could be a hint that the system transforms from amorphous carbon to nanocrystalline carbon.\(^{[14]}\) A more detailed analysis of the G peak position and the intensity ratio follows in Section 3.1.4.

### 3.1.2. Tannin

In the temperature-dependent spectra of tannin, which are shown in Figure 2, only the spectra of the samples preannealed...
to 400 °C and higher are displayed. The spectra at RT, 100 °C, and 200 °C exhibit a very high PL background obscuring all Raman signals. For amorphous carbon systems, this is a hint that the hydrogen content is higher than 40%.\(^{15}\) Similar to Carbores P, the PL background decreases with growing temperatures until there is no more observable background at 800 °C, which means the hydrogen content is below 20%.

At 400 °C, shoulders at 1170 and 1450 cm\(^{-1}\) can be seen, which, again, can be assigned to trans-PA.\(^{31,32}\) The peak at 585 cm\(^{-1}\) and the shoulder at 1630 cm\(^{-1}\) could originate from an in-plane bending of three carbon atoms C—C—C (it is also possible to substitute one or two C with O) and a C—C stretching vibration in the nonpyrolyzed tannin molecules, respectively.\(^{37-39}\)

At 1000 °C, a small peak at 1081 cm\(^{-1}\) appears. This peak can be attributed to carbonate species, such as CaCO\(_3\)\(^{40,42}\) or Na\(_2\)CO\(_3\)\(^{43}\) both of which exhibit a very intense peak around 1080 cm\(^{-1}\).

At higher temperatures, features such as the sharp G peak at 1585 cm\(^{-1}\), which is still partly overlaid by the G peak of the amorphous carbon, as well as the clear second order peak at 2705 cm\(^{-1}\)\(^{30,44}\) appear, indicating the transition of amorphous carbon to nanocrystalline graphite. The transition will be discussed in more detail later.

Similar to Carbores P, the high-temperature spectra (800–1400 °C) show a lower intensity compared to the spectra for lower temperatures. This observation can be explained by a smaller optical gap and increasing absorption for lower sp\(^3\) content, leading to a lower penetration depth of the laser light and consequently a lower scattering volume.\(^{14}\)

### 3.1.3. Lactose

The spectra of the lactose samples show very similar trends to the spectra of tannin and Carbores P and are therefore not shown in this article.

At RT and 100 °C, the lactose spectra show no G or D peak, but rather various “fingerprint” peaks below 1500 cm\(^{-1}\) and in the range of 2700–3600 cm\(^{-1}\). These peaks are in very good agreement with the literature.\(^{45,46}\) At 200 °C, conversion to amorphous carbon occurs, leading to high PL in the Raman spectra and then to the characteristic G and D peaks for temperatures of 400 °C and above.
3.1.4. Discussion of $I_D/I_G$ Ratio and G Position

The intensity ratio of the D and G peaks $I_D/I_G$ as well as the position of the G peak gives us valuable information on the investigated carbon system. To get the intensities and positions of the D and G peaks, the peaks were fitted with a Lorentzian and a Breit–Wigner–Fano (BWF) function, respectively. This approach is, apart from the fit with Gaussians,[13] the most common one.[14,47] The shoulders assigned to trans-PA were fitted with Gaussians.

The BWF function has an asymmetric line shape attributed to the coupling of a discrete mode with a continuum.[48] Put more precisely, the discrete phonon spectra interfere with the continuous one-particle electron–hole pair spectra.[49] The BWF function $I_{\text{BWF}}$ for a given Raman peak[14,47,49] is defined as

$$I_{\text{BWF}}(\omega) = I_0 \left( 1 + \frac{2(\omega_0-\omega)^2}{Q^2 b^2} \right) \left( 1 + \frac{2(\omega_0-\omega)^2}{Q^2 b^2} \right)$$  \hspace{1cm} (2)

wherein $I_0$ is the intensity maximum, $b$ is the full width at half maximum (FWHM), $\omega_0$ is the peak position, and $Q$ is the BWF coupling coefficient. Because of the asymmetry on the right-hand side of Equation (2), the position of $I_0$, termed $\omega_{\text{max}}$, is not identical to the peak position $\omega_0$. Instead, $\omega_{\text{max}}$ is given by

$$\omega_{\text{max}} = \omega_0 + \frac{b}{2Q}$$  \hspace{1cm} (3)

In the following, we refer to $\omega_{\text{max}}$ whenever we mention the position of the G peak.

The fit process is shown in Figure 3, specifically in the upper left corner. For the background correction before the actual fit, the asymmetric least-squares method developed by Eilers and Boelens[56] was used (parameter choice: $p = 10^{-1}$ for asymmetry and $\lambda = 10^2$ for smoothness; both of these values are within the ranges recommended by the authors, i.e., $[10^{-3}, 10^{-1}]$ for $p$ and $[10^2, 10^3]$ for $\lambda$).

In Figure 3, the determined $I_D/I_G$ values (upper half) and the positions of the G peak (lower half) are shown. For each sample, at least five measurements were performed. In Figure 3, the mean values of these measurements are displayed and the error bars represent the respective standard deviations.

For lactose and tannin, the values could not be estimated below temperatures of 400 and 600 °C, respectively. In the case of lactose, this is because the spectra exhibited neither a D nor a G peak, indicating that the molecular structure was still intact. In the case of tannin, the analysis was prevented by the strong PL.

Because all three series (Carbores P, lactose, and tannin) show similar trends, they are covered in one discussion. Up to temperatures of 600 °C, the intensity ratios and G positions remain nearly the same, indicating no significant changes in the structure and composition of the sample. The system can be classified as hydrogenated amorphous carbon (a-C:H), containing ring-like and chain-like carbon (e.g., trans-PA; compare the previous discussion of Figure 1) as well as $sp^3$-hybridized carbon.[14]

For amorphous carbon, the intensity ratio of the D and G peaks $I_D/I_G$ depends on the number of ordered carbon rings and the size of the graphitic carbon cluster they constitute. The cluster size in the $ab$ plane $L_a$ can be estimated using the following relation[14,29]

$$\frac{I_D}{I_G} = \frac{C(\lambda)L_a^2}{L_a^2}$$  \hspace{1cm} (4)

Here, $C(\lambda)$ is a wavelength-dependent constant with the value of 0.55 nm$^{-2}$ for a wavelength of 514 nm,[14] which is considered close enough to the used wavelength of 532 nm. The sizes of the $sp^2$ carbon clusters shown in Figure 4 stay roughly the same up to 600 °C.

Between 600 and 1000 °C, $I_D/I_G$ increases, indicating a change from amorphous carbon to nanocrystalline graphite. This corresponds to a growth of $sp^2$ carbon clusters, whereas...
the percentage of $sp^3$ and chain-like carbon as well as the hydrogen content decreases. These processes are consistent with the registered intensity drop, the absence of the trans-PA peaks at 1170, 1240, and 1450 cm$^{-1}$, and the disappearance of PL as discussed earlier (compare Figure 1 and 2).

For nanocrystalline graphite, a new relation between the intensity ratio and the $sp^2$ carbon cluster size applies, which leads to opposite trends compared to amorphous carbon.$^{8,14}$ In this new relation, $I_D/I_G$ is inversely proportional to the cluster size $L_a$, following the empirical Tuinstra–Koenig equation$^{28}$

$$
\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a}
$$

with $C$ (514 nm) = 4.4 nm. For a more detailed evaluation of the D/G peak ratios, additional measurements at ultraviolet wavelengths have been recommended in the literature.$^{14}$

At 1400 °C $I_D/I_G$ and the G position decrease again for tannin and Carbores P, indicating a growth of the $sp^2$ carbon cluster areas (Figure 4). These findings are in good agreement with earlier reports.$^6,8$ At 1400 °C, the average cluster sizes as calculated with Equation (5) are around 5.1 nm for Carbores P and 4.6 nm for tannin. The large error bar at 1400 °C stems from an inhomogeneous distribution of cluster sizes across the sample. It appears as if the $sp^2$ carbon clusters have merged at some points in the sample, and at other points they have not. Dopita et al. investigated the structural changes of Carbores P with X-ray diffraction (XRD),$^{51}$ and their conclusions regarding cluster size and cluster size distribution are in good agreement with the presented results.

For lactose, the values of the G position and the intensity ratio keep increasing at 1400 °C, and therefore the cluster size decreases. These findings are in contrast to those for tannin and Carbores P. A reason for this difference in behavior could be that the lactose samples were building a foamy structure during the heating process, whereas the Carbores P and tannin samples had a fine-grained one.
3.2. Carbon-Bonded Alumina Samples

3.2.1. Raman

The recorded spectra of the carbon-bonded alumina samples show significant differences depending on the measurement point on the sample surface. Figure 5 shows an image of the sample surface taken through an optical microscope with 50× magnification. There are two distinguishable types of areas, bright silver flakes and a gray matrix part, which can be divided into a light gray and a dark gray section. In Figure 5, examples of the different areas are marked by a thin black contour. Figure 5 also shows the corresponding spectrum for each type of area.

The spectra measured at the silver flakes all exhibit a very strong G peak around 1580 cm\(^{-1}\). In contrast, the D peak is barely pronounced at all, which indicates the silver flakes are highly ordered graphite. The amount of sample surface area that is occupied by the silver flakes is in good agreement with the percentage of the added graphite, i.e., 7.7% (compare Table 2). This is confirmed by the strong distinct second order peaks around 2450, 2720, and 3240 cm\(^{-1}\).[30,52,53]

The dark gray matrix spectra display the D peak in addition to the G peak, indicating the presence of disorder in this part of the sample. The second order peaks vanish, and a broad band in the range between 2400 and 3100 cm\(^{-1}\) can be seen instead, which is typical for amorphous carbon systems.

The light gray matrix spectra exhibit a strong PL background originating from a high hydrogen content visible in the corresponding Raman spectrum. In fact, the PL background nearly covers the Raman signal. This is known to occur for excitation in the visible range if the hydrogen content is above 40–45 at%.[35]

Using the same procedure that was applied to Carbores P, lactose, and tannin, the positions of the G peaks and the intensity ratios \(I_D/I_G\) were determined. In Figure 6, the results of these evaluations are plotted against each other. Three data groups can be distinguished. The first group, with a low G position and intensity ratio, is associated with the silver graphite flakes. For perfect graphite, \(I_D/I_G \rightarrow 0\) and the G position is around 1580 cm\(^{-1}\). For nanocrystalline graphite, both values increase.

For the silver flakes, only the lower limit of the graphitic cluster size can be estimated as 20 nm because the Tuinstra–Koenig equation (Equation (5)) is valid only below this limit.[29] The firing of the samples has no detectable influence on the cluster sizes within the silver graphite flakes. Additionally, we cannot observe any differences between the samples with different Carbores P to lactose/tannin ratios, or between the samples with and without n-Si.

The second group (0.5 < \(I_D/I_G\) < 0.7 and 1582 cm\(^{-1}\) < G position < 1594 cm\(^{-1}\)) corresponds to measurements taken on the dark gray matrix part of unfired samples (series A and B). Based on our knowledge of the raw materials and the findings from the measurements on Carbores P, tannin, and lactose, the dark gray matrix part of the unfired samples can be classified as amorphous carbon. The larger variation in the data compared to the silver graphite flakes can be explained by the inhomogeneity of the samples. Again, the composition and whether Si was added or not seem to have no influence that can be detected with Raman spectroscopy.

The third group contains values obtained from the light gray matrix spectra and the dark gray matrix spectra of the fired sample. Due to the heat treatment, the intensity ratios as well as the G positions increase, which is why this group is found in the upper right corner of Figure 6. The values are in good agreement with the values measured for Carbores P, tannin, and lactose at 1000 °C (compare Figure 3).

The position of the G peak in the fired samples with added n-Si seems to have a larger variation compared to the fired samples without n-Si. A reason could be that the silicon grains interact with the carbon in their immediate vicinity.

3.2.2. Carbon Yield

Apart from the structural arrangement of the carbon, the total carbon content in the samples after firing is important for the

![Figure 6. D/G peak intensity ratios plotted against the G positions of the carbon-bonded alumina samples.](image-url)
filter properties. Table 3 shows the carbon content of the fired filter samples with and without n-Si.

The percentage of carbon in the samples correlates with the amount of added Carbores P. This is in line with a lower carbon loss of Carbores P, which achieves a carbon yield of 83% after firing according to the supplier. In comparison, the carbon yield of lactose/tannin after firing is much lower.[7,8]

The added n-Si seems to exert no considerable impact on the carbon yield in case of the binders lactose/tannin and Carbores P. This is in contrast to novolak binders, which have shown a higher carbon yield with added n-Si.[10]

4. Conclusion

Environmentally friendly binder systems for carbon-bonded alumina filters were investigated by Raman spectroscopy. Measurements on preannealed samples of the pure binders Carbores P, tannin, and lactose showed that the samples underwent a change from hydrogen-rich amorphous carbon to nanocrystalline carbon during firing. Studying the thermal changes in \( I_D / I_G \) and the G peak position revealed a growth of the sp\(^3\) carbon cluster areas with increasing temperature.

In addition, spectra of carbon-bonded alumina filter samples with different binder compositions and with or without n-doped silicon were analyzed. The samples exhibited an inhomogeneous surface, which could be distinguished in a dark and light gray matrix portion and silver graphite flakes. The graphite added to the filter as one of the carbon sources showed no changes due to heat treatment or the presence of n-Si. The \( I_D / I_G \) ratios and the G positions of the matrix part displayed a similar dependence on the firing temperature as the pure binders. The G positions of the samples containing n-Si showed a larger variance than the samples without n-Si, which could hint at an influence of silicon on graphitization.

Between the different binders Carbores P, tannin, and lactose, Raman spectroscopic measurements performed in this study could not find any significant differences after heat treatment. This means that from this point of view, it is possible to reduce the amount of benzo[a]pyrene containing Carbores P because lactose/tannin are equally well suited.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

ceramic foam filters, lactose, Raman spectroscopy, tannin

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