Preparation of Cerium-Bismuth Oxide Catalysts for Diesel Soot Oxidation Including Evaluation of an Automated Soot-Catalyst Contact Mode

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Cerium-bismuth oxides have emerged as promising candidates for Diesel soot oxidation. The catalysts are synthesized via automated co-precipitation methods. T_{50} values, where 50% of soot is oxidized, and the dynamic oxygen storage capacity (OSC_{dynam}) are used to compare the catalytic activity. The activity is measured by thermogravimetric methods. The synthesized catalysts are characterized through powder X-ray diffraction (PXRD), Raman spectroscopy, and specific surface area (S_{BET}) measurements. This work investigates the influence of the contact mode between soot and catalyst. The literature-known manual contact modes “loose”, “tight”, and “wet” are compared with our developed automated contact mode, using a dual asymmetric centrifuge. The rotation speed rs and mixing time tm have been varied independently. Both factors influence the T_{50} value. A continuous transition from loose to tight contact mode with increasing rotation speed rs can be shown. Furthermore, the automated contact mode shows better reproducibility behavior compared to manual contact modes.

Introduction

The World Health Organization classifies Diesel soot as carcinogenic.[1] Diesel soot is suspected to cause lung or cardiovascular diseases.[2, 3] Furthermore, Diesel soot influences the atmospheric visibility, soiling of buildings, the vegetation, or the climate due to its optical properties depending on particle size, shape, and composition.[4] Nevertheless, Diesel cars are popular because of more efficient engines, better fuel economy, and lower emissions of HC, CO, and CO_{2}. Contrary to gasoline engines, Diesel engines emit higher quantities of NO, and the so-called soot. Both pollutants are restricted by vehicle emission standards.[5] Therefore, different exhaust gas post-treatment technologies are established. For example, Diesel particulate filters (DPF) remove soot from the exhaust gas stream.[6, 7] Over time, the Diesel soot collected accumulates in the DPF. As a consequence, the backpressure of the exhaust gas post-treatment system rises and leads to higher fuel consumption because of filter regeneration processes or even to filter failure.[8, 9] In the event that the pressure threshold of the DPF is reached, the DPF has to be regenerated. Mainly, there are two regeneration approaches: active and passive regeneration.[10] During the passive regeneration process, the accumulated soot is continuously oxidized by a catalytic chemical reaction utilizing residual oxygen in the off-gas stream. The activity is measured by thermogravimetric methods. The synthesized catalysts are characterized through powder X-ray diffraction (PXRD), Raman spectroscopy, and specific surface area (S_{BET}) measurements. This work investigates the influence of the contact mode between soot and catalyst. The literature-known manual contact modes “loose”, “tight”, and “wet” are compared with our developed automated contact mode, using a dual asymmetric centrifuge. The rotation speed rs and mixing time tm have been varied independently. Both factors influence the T_{50} value. A continuous transition from loose to tight contact mode with increasing rotation speed rs can be shown. Furthermore, the automated contact mode shows better reproducibility behavior compared to manual contact modes.

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that influence the repeatability of the measurements. To overcome this problem, Hensgen et al. developed the "wet" contact. The wet contact is an intimate contact and determined by dispersing soot and catalyst in a dispersion agent. Acetone has proven to be the best candidate as dispersion agent. Hensgen et al. used nano-

calculated CeO₂ as catalyst with different types of model soot. In their study, a good measurement repeatability was achieved. 

In the present paper, the loose, tight, and wet contact modes are compared using PXRD, Raman spectroscopy, XRF, S_{\text{BET}}, and OSC_{\text{dyn}} measurements. Furthermore, an automated contact mode with a dual asymmetric centrifuge is developed to exclude any manual influence using a commercial device. The T_{10} values serve to compare the activities measured by an automated thermal gravimetric analysis method.

**Results and Discussion**

**Catalyst Characterization**

XRF measurements shown in Table 1 were performed to verify the nominal Bi and Ce percentages of the co-precipitated BiCeO samples (Bi:Ce = 1:1). The oxygen content is not included in the presented results because the detector does not allow the quantification of oxygen. The mass percentages of Bi and Ce of the BiCeO samples which are precipitated by the precipitants ammonium carbonate (AC) and oxalic acid (OA) differ not more than Δm% = 3% between nominal and experimental received values.

Table 2 presents the results of the specific surface area S_{\text{BET}} and the dynamic oxygen storage capacity OSC_{\text{dyn}} measurements. S_{\text{BET}} was determined through N₂ physisorption experiments and by the multi-point BET method. The reference sample AdNanoCeria supplied by Evonik Degussa produced through flame spray pyrolysis has the highest S_{\text{BET}} = 60 m²·g⁻¹ and highest OSC_{\text{dyn}} = 42 μmol₂·g⁻¹·mol⁻¹ compared to co-precipitated samples. The pure CeO₂ precipitated by AC solution has a lower S_{\text{BET}} = 27 m²·g⁻¹ as well as lower OSC_{\text{dyn}} = 25 μmol₂·g⁻¹·mol⁻¹ compared to AdNanoCeria. In comparison, the pure CeO₂ precipitated by OA shows an even smaller specific surface with S_{\text{BET}} = 4 m²·g⁻¹. On the other hand, the standard deviation of the OSC_{\text{dyn}} relative to its absolute value of the CeO₂·OA is very high with OSC_{\text{dyn}} = 5 ± 4 μmol₂·g⁻¹·mol⁻¹ and implies an inhomogeneous sample with respect to the distribution of oxygen vacancies and redox ability. A reverse trend was shown by the BiCeO samples. The BiCeO.AC has a smaller surface area of S_{\text{BET}} = 8 m²·g⁻¹ compared to BiCeO.OA. On the contrary, the BiCeO precipitated by OA has a S_{\text{BET}} = 15 m²·g⁻¹, but the OSC_{\text{dyn}} is higher for BiCeO.AC compared to BiCeO.OA (OSC_{\text{dyn}} = 25 μmol₂·g⁻¹·mol⁻¹ versus OSC_{\text{dyn}} = 6 μmol₂·g⁻¹·mol⁻¹).

**PXRD and Raman Spectroscopy**

Figure 1 shows the PXRD patterns of the reference sample AdNanoCeria and the co-precipitated samples. In general, the PXRD patterns of the samples precipitated by OA reveal higher FWHM (full width at half maximum) of the reflections compared to the samples precipitated by AC, especially for the sample BiCeO.OA indicating lower crystallite size. The samples AdNanoCeria, CeO₂.AC and CeO₂.OA crystallize in a cubic fluorite-type structure with space group Fm3m. Table 3 presents the results of Rietveld refinements.

Both BiCeO samples consist of more than one crystalline phase. According to Rietveld refinements, the BiCeO.OA sample consists of three different crystalline phases with exclusive Bi³⁺ occupation on cation positions. These are the monoclinic α-Bi₂O₃ phase with space group P2₁/c, the tetragonal β-Bi₂O₃ phase with space group P4₂₁c, and the orthorhombic bismuthite Bi₅(CO₃)₂O₂ phase with space group Imm2. For the BiCeO.AC sample, an amount of only m = 2.7 wt% of bismuthite is refined. Due to a detailed reflection profile analysis in the course of the Rietveld refinement, two cubic CeO₂ phases with different lattice parameters are identified in the BiCeO samples. One cubic fluorite-type phase is CeO₂ doped with Bi⁵⁺ and the other phase is pure CeO₂. This finding might be explained by the presence of domains of the CeO₂ phase with varying Bi⁵⁺ content due to substitution of Ce⁴⁺ by Bi³⁺. The Bi³⁺ doped CeO₂ phases in the samples BiCeO.AC and BiCeO.OA have larger lattice parameters a = 5.4362(2) Å and a = 5.4237(3) Å compared to pure AdNanoCeria with a = 5.4082(1) Å. The substitution of Ce⁴⁺ by Bi³⁺ is accompanied by oxygen lattice defect formation of Frenkel-type as indicated by Equation (1) (in Kröger–Vink notation):

\[
\text{Bi}_{\text{bi}}\text{O}_{\text{ce}}(\text{CeO}_2) = 2\text{Bi}^{3+} + \text{V}_{\text{Ce}}^{\text{a}} + 3\text{O}^6_{\text{aq}}
\]  

Figure 2 shows the Raman spectra of the oxides used or prepared in this work. AdNanoCeria, CeO₂.AC, and CeO₂.OA all reveal the typical band at ν = 462 cm⁻¹ which is the triply degenerate F₂g mode that corresponds to a symmetric Ce−O
Figure 1. Powder X-ray diffraction (PXRD) pattern of co-precipitated BiCeO and CeO$_2$ with different precipitants and calcination at $T = 800^\circ$C as well as the reference sample AdNanoCeria. (a) PXRD measured with Co-K$_\text{\textalpha}$ radiation, $\lambda = 1.7892$ Å. (b) PXRD measured with Cu-K$_\text{\textalpha}$ radiation, $\lambda = 1.5406$ Å. Following reference files are used: CeO$_2$: ICDD #75–76; $\alpha$-Bi$_2$O$_3$: ICDD #71–2274; $\beta$-Bi$_2$O$_3$: ICDD #78–1793.

Table 3. Results of Rietveld refinement of the reference sample AdNanoCeria measured with Cu-K$_\text{\textalpha}$ radiation, $\lambda = 1.5406$ Å and the co-precipitated samples measured with Co-K$_\text{\textalpha}$ radiation, $\lambda = 1.7892$ Å. Co-precipitated samples are calcined at $T = 800^\circ$C.

| Sample          | AdNanoCeria | CeO$_2$ AC | BiCeO AC | CeO$_2$ OA | BiCeO OA |
|-----------------|-------------|------------|----------|------------|----------|
| CeO$_2$ [w%]    | 100         | 100        | 46(2)    | 100        | 62.1(12) |
| a [Å]           | 4.4082(1)   | 5.4109(5)  | 5.415(4) | 5.4115(2)  | 5.4234(3) |
| Crystal size L [nm] | 55.9(5)    | 46.5(2)    | 22.2(3)  | 15.2(1)    | 11.1(1)  |
| (Ce,Bi)O$_2$ [w%] |             |            |          |            |          |
| a [Å]           | 5.436(2)    |            |          |            |          |
| sof$_\text{Ce}$ [%] |            | 63.3(2)    |          |            |          |
| sof$_\text{Bi}$ [%] |            | 36.7(2)    |          |            |          |
| Crystal size L [nm] |            |            | 26.2(4)  |            |          |
| Bi$_2$(CO$_3$)O$_2$ [w%] |         |            | 2.7(1)   |            |          |
| a [Å]           | 5.47(3)     |            |          |            |          |
| b [Å]           | 27.4(1)     |            |          |            |          |
| c [Å]           | 5.45(5)     |            |          |            |          |
| Crystal size L [nm] |            |            | 33(2)    |            |          |
| $\beta$-Bi$_2$O$_3$ [w%] |         |            |          |            |          |
| a [Å]           | 5.59(5)     |            |          |            |          |
| c [Å]           | 7.7406(4)   |            |          |            |          |
| Crystal size L [nm] |            |            | 0.89(4)  |            |          |
| $\alpha$-Bi$_2$O$_3$ [w%] |         |            | 5.0(5)   |            |          |
| a [Å]           | 5.8494(5)   |            |          |            |          |
| b [Å]           | 8.1632(6)   |            |          |            |          |
| c [Å]           | 7.5106(7)   |            |          |            |          |
| $\beta$ [$^\circ$] |            |            | 112.995(7) |          |
| Crystal size L [nm] |            |            | 330(60)  |            |          |
| $R_{wp}$        | 4.190       | 5.068      | 4.939    | 5.820      | 6.237    |
These bands are observed at the frequencies $\nu = 126, 229, 314, 460, 512, 575,$ and $1152\, \text{cm}^{-1}$. The bands at $\nu = 126, 229, 314\, \text{cm}^{-1}$ clearly refer to $\beta$-Bi$_2$O$_3$. Note that the band at $\nu = 460\, \text{cm}^{-1}$ can be assigned to both the $F_{2g}$ mode of the CeO$_2$ lattice or $\beta$-Bi$_2$O$_3$.\cite{37,40,41} Like in the Raman spectra for BiCeO$_{AC}$, there are the two broad bands at $\nu = 512$ and $575\, \text{cm}^{-1}$ according to oxygen vacancies of the CeO$_2$ lattice. The band at $\nu = 1152\, \text{cm}^{-1}$ is again due to the vibration of O$_2^-$ group.\cite{37}

According to Bao et al., the intensity ratio $I_{514}/I_{460}$ of the bands at $\nu = 464$ and $595\, \text{cm}^{-1}$ is to be calculated to get a better comparison of the relative concentration of the defect complexes of the BiCeO$_2$ samples.\cite{42} The intensity ratio $I_{514}/I_{460}$ of BiCeO$_{AC}$ is 0.68(2) and that of BiCeO$_{OA}$ amounts to 0.33(2). Therefore, the amount of defects in BiCeO$_{AC}$ is higher than in BiCeO$_{OA}$.

**Activity Measurements**

**Repeatability Behaviors of Different Contacts**

The activity measurements are conducted with a serial thermogravimetric and differential scanning calorimetry system (TGA/DSC). The repeatability behaviors of the loose, tight, wet contact modes, and our development, the automated contact were investigated with nano-scaled AdNanoCeria, CeO$_2$,$_{AC}$ and CeO$_2$,$_{OA}$ as sample materials. The samples are calcined at $T = 800\, ^\circ\text{C}$ to avoid any changes of the crystal structure during the reaction in a temperature range of $T = 25$–700 $^\circ\text{C}$ and to improve the crystallinity of the samples. Piumetti et al. investigated the influence of different CeO$_2$ crystal structures. They determined that calcination temperatures above $T > 500\, ^\circ\text{C}$ produces more active sites of the CeO$_2$ samples.\cite{43} Hueso et al. showed that grinding their catalyst, a $\text{La}_2\text{Sr}_2\text{CeO}_6$,$_3$ perovskite, and soot together can cause a partially reduction of Co$^{3+}$ to Co$^{2+}$.\cite{44} In the present investigation, we do not observe such an effect. Figure 3 shows the TGA curves measured for different contact modes between soot and catalyst with constant weight ratio of 1:4. AdNanoCeria60 was used for the activity measurements. Each gravimetric activity measurement was repeated five times. Considering Figure 3, loose and tight contact mode have problems of repeatability compared to wet and automated contact.

To compare the repeatability, the average and the standard deviation of the relative weight loss $\Delta m/m_0$ and $\sigma(m/m_0)$ can be used. The value $\Delta m/m_0$ should be close to $\Delta m/m_0 = 20\%$ (catalyst:soot = 4:1) and $\sigma(m/m_0)$ should be as low as possible. The obtained values are listed in Table 4. On the other hand, the $T_{50}$ value is a good indicator of contact tightness: as the soot combustion is only occurring at the direct contact area between soot and catalysts, lower $T_{50}$ values represent a more intimate contact between both components. The loose contact mode has the highest $T_{50}$ value of $T_{50} = 631\pm6\, ^\circ\text{C}$. On the other side, the automated contact possesses the lowest $T_{50}$ value of $T_{50} = 436\pm2\, ^\circ\text{C}$. The relative weight loss $\Delta m/m_0$ is in the same range of $\Delta m/m_0 = 21.5\%$ for all contact modes. The loose contact has the highest standard deviation of the relative
weight loss with \(\sigma(m/m_0) = 1.9\%\). The 5th repetition of this series (brown line) might be considered as an outlier, but is quite commonly observed for loose contact due to sample inhomogeneities (see below). This implicates that the loose contact has the lowest repeatability. The \(\sigma(m/m_0)\) of the tight, wet, and automated contact are below \(\sigma(m/m_0) = 1\%\). These values indicate good repeatability behavior.

In contrast to AdNanoCeria, for example CeO\(_2\) precipitated by AC reveals different properties, see Figure 4 and Table 5. The loose contact mode shows a poor repeatability behavior and the highest \(T_{50}\) value with \(T_{50} = 652 \pm 2\,^\circ\text{C}\). The average and deviation of the relative weight loss of soot is \(\Delta m/m_0 = 27\%\) and \(\sigma(m/m_0) = 12\%.\) \(\Delta m/m_0\) is approximately 7% higher than the theoretical relative weight loss of soot, indicating a rather inhomogeneous soot-catalyst mixture.

The wet contact mode seems to break into two different soot-catalyst mixtures, one mixture containing more and the other less soot. Compared to AdNanoCeria, CeO\(_2\) AC might have a broad or even bimodal particle size distribution and
during the wet contact preparation despite intense stirring, there is a separation of particles of different size and thus also of the amount of soot connected to the catalyst’s fractions. The tight contact has the lowest $T_{50}$ value with $T_{50} = 621 \pm 1 \degree C$. The difference from the theoretical relative weight loss is quite low with $\Delta m/m_0 = 18.5 \pm 0.1 \%$. The standard deviation is much smaller than 1 %, indicating good repeatability behavior as well as a homogeneous soot-catalyst mixture. The automated contact has a $T_{50} = 632 \pm 3 \degree C$, lying in between the loose and tight contact mode. As will be shown later, the automated mode offers the possibility to adjust the contact tightness by experimental parameters. The relative weight loss of soot is again quite close to the theoretical value with $\Delta m/m_0 = 19 \pm 4 \%$. But the standard deviation of the relative weight loss is $\sigma(m/m_0) = 4 \%$ and thus higher than that of the tight contact mode, but better compared to the loose contact mode. As the automated contact is prepared by mixing soot and catalyst in a dual asymmetric centrifuge at rotating conditions rotation speed $n = 3500 \ rpm$ and mixing time $t_m = 300 \ s$.  

Table 6 presents the results of $T_{50}$ and $\Delta m/m_0$ measurements for the CeO$_2$-OA sample. It can be seen that the loose and wet contact mode have the highest $T_{50}$ values with $T_{50, Loose} = 651 \pm 1 \degree C$ and $T_{50, Wet} = 640 \pm 10 \degree C$. In this case, the $\Delta m/m_0$ values are $20.7 \pm 5.7 \%$ and $26.6 \pm 10.2 \%$, respectively. However, the automated contact mode has the lowest $T_{50}$ value of $625 \pm 3 \degree C$ with a $\Delta m/m_0$ of $17.9 \pm 1.0 \%$.

**Table 6.** $T_{50}$ values and relative weight loss $\Delta m/m_0$ of soot during activity measurements determined by TGA measurements. CeO$_2$-OA was used as catalyst in a weight ratio of 4:1 of catalyst and soot. The averages and their standard deviations of five repeated measurements are shown. Automated contact realized by the dual asymmetric centrifuge at rotating speed $n = 3500 \ rpm$ and mixing time $t_m = 300 \ s$.

| Contact mode | $T_{50}$ [\degree C] | $\Delta m/m_0$ [%] |
|--------------|----------------------|---------------------|
| Loose        | 651.0 ± 1.3          | 20.7 ± 5.7          |
| Tight        | 636.2 ± 2.0          | 20.3 ± 0.3          |
| Wet          | 640.0 ± 9.6          | 26.6 ± 10.2         |
| Automated    | 625.0 ± 3.1          | 17.9 ± 1.0          |

Figure 4. TGA curves of repeatability measurements of different contact modes between soot and CeO$_2$-AC as catalyst calcined at $T = 800 \degree C$. Weight ratio between catalyst and soot is 4:1. Measurements are performed by TGA-DSC system with temperature range $T = 25$–$700 \degree C$ and heating rate $r = 5 \degree C \cdot min^{-1}$ in synthetic air flow $V = 25 \ mL \cdot min^{-1}$. The following contact modes are shown: (a) loose contact; (b) tight contact; (c) wet contact with dispersion agent acetone; and (d) automated contact realized by the dual asymmetric centrifuge at operating conditions rotation speed $n = 3500 \ rpm$ and mixing time $t_m = 300 \ s$. 

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automated contact mode has the lowest $T_{50} = 625 \pm 3\,^\circ C$. With respect to repeatability behavior, the loose and wet contact mode have much higher standard deviations of the relative soot weight loss compared to the other two contact modes. This indicates homogeneous soot-catalyst mixtures and good repeatability behavior of tight and automated contact modes.

All in all, the automated contact shows good repeatability behavior according to the relative weight loss of soot. The $T_{50}$ values achieved with the automated contact are in the range of the tight contact mode but the contact tightness can be adjusted by operational parameters as will be shown in the next chapter. It is noteworthy that the contact modes are influenced by specific properties of the samples and the fact that soot and catalyst have rather different surface polarities and energies. This makes the contact of the two components prone to demixing effects, additionally enforced by contact with accessories during the mixing process.

### Further Investigation of the Automated Contact Mode

The automated contact was realized with a dual asymmetric centrifuge for a number of other samples, too. The investigation of operating conditions of the centrifuge are described in more detail in this section. The rotation speed $rs$ was varied between $rs = 300–3500$ rpm in $\Delta rs = 200$ rpm steps and the mixing time was held constant at the two levels of $t_m = 60$ s and $t_m = 300$ s. The influence of $rs$ at $t_m = 60$ s was investigated for all samples. The results are shown in Figure 5 and Table 7.

Based on the TGA curves and $T_{50}$ values presented in Figure 5 and Table 7, there is a clear trend for all samples. With increasing rotation speed $rs$ the TGA curves shift to lower temperatures and the $T_{50}$ values decrease. The sample CeO$_2$-OA does not follow the trend of the other samples. Here, the problem is the low activity for soot oxidation due to both low $S_{BET}$ and low OSC$_{dyn}$. The largest effect of increasing $rs$ is seen for the AdNanoCeria60 sample in agreement with the by far highest $S_{BET}$ and highest OSC$_{dyn}$ within the samples investigated resulting in good activity for the soot oxidation reaction. For further explanation of the results, the particle size distributions measured by static light scattering were used, represented in Figure 6. The samples AdNanoCeria, CeO$_2$-AC and BiCeO$_2$-AC possess a broad particle size distribution. Especially, in the range of hydrodynamic diameter $d_h$ below $d_h = 10\,\mu m$ there are more particles available in these samples. For the samples precipitated by oxalic acid, the particles are more narrowly distributed around the maximum hydrodynamic diameter of $d_h \approx 11\,\mu m$ and there are not many particles with sizes below $d_h = 10\,\mu m$. Table 7 shows the $T_{50}$ values at different rotation speeds. The highest difference of combustion temperature between the loose contact-like condition at $rs = 300$ rpm and the tight contact at $rs = 3100$ rpm is achieved by the nano-scaled AdNanoCeria60 with $\Delta T_{50} = 213\,^\circ C$. The shift of $T_{50}$ values is greater for the samples precipitated by AC than for those precipitated by OA. The $\Delta T_{50}$ values of BiCeO$_2$-AC and CeO$_2$-AC are $\Delta T_{50} = 57\,^\circ C$ and $\Delta T_{50} = 77\,^\circ C$, respectively. On the other hand, BiCeO$_2$-OA and CeO$_2$-OA have a shift of $T_{50}$ values of only $\Delta T_{50} = 10\,^\circ C$ and $\Delta T_{50} = 45\,^\circ C$ to lower temperatures, respectively. Furthermore, the BiCeO$_2$-AC has, at the lowest rotation speed of $rs = 300$ rpm, the lowest $T_{50}$ Value of $T_{50} = 539 \pm 1\,^\circ C$, indicating the best activity towards soot oxidation at loose contact conditions.

In Figure 7, the $T_{50}$ values of the samples used in this work are compared at different rotation speeds $rs$. As already described above, the nano-scaled AdNanoCeria60 has the greatest shift of $T_{50}$ values and the lowest $T_{50}$ value of $T_{50} = 394 \pm 1\,^\circ C$ at $rs = 3100$ rpm. The BiCeO$_2$-AC shows the best catalytic activity of the precipitated samples with lowest $T_{50}$ value of $T_{50} = 482 \pm 1\,^\circ C$ at $rs = 2100$ rpm. The CeO$_2$-OA sample shows the lowest activity towards soot oxidation and the lowest $\Delta T_{50}$ value.

The next step was to investigate the influence of the mixing time $t_m$. Experiments are performed with the AdNanoCeria60 and the BiCeO$_2$-OA samples at two different mixing times of $t_m = 60$ s and $300$ s. The resulting $T_{50}$ values on variation of $rs$
are shown Figure 8 and Table 8. The influence of the mixing time $t_M$ of 300 s decreases the $T_{50}$ values. The difference of $T_{50}$ values is not more than $\Delta T_{50} = 25^\circ C$ at $r_s = 1100$ rpm. At rather high mixing rates of $r_s = 2700$ rpm and above, the $T_{50}$ differences decrease again to $\Delta T_{50} = 7^\circ C$. Furthermore, the lowest $T_{50}$ is observed at $r_s = 3000$ rpm. Further increasing of $r_s$ leads to a small increase of $T_{50}$ value. For the BiCeO_OA sample, the greatest difference between the $T_{50}$ values is observed at a rotation speed $r_s = 3500$ rpm with $\Delta T_{50} = 10^\circ C$, indicating the minor influence of mixing time towards $T_{50}$ values.

Figure 5. TGA curves from the investigation of the rotation speed $r_s$ for the automated contact mode. Measurements are performed by TGA-DSC system with temperature range $T = 25–700^\circ C$ and heating rate $r = 5^\circ C\cdot min^{-1}$ in synthetic air flow $V = 25 mL\cdot min^{-1}$. Catalyst-soot weight ratio is 4:1. Mixing time $t_M = 60$ s. The following catalysts are shown: (a) AdNanoCeria60; (b) CeO$_2$_AC; (c) CeO$_2$_OA; (d) BiCeO_OA; (e) BiCeO_OA.
Figure 6. Histogram of the particle size distribution (PSD) of samples used in this work and determined by a static light scattering method. Five repeated measurements were recorded for each sample and all samples were treated with ultrasonic irradiation for t = 60 s before measurement. Every 5th measurement of the samples is shown.

Figure 7. Comparison of soot oxidation T_{50} values and standard deviations of different catalysts in automated contact mode with mixing time t_{mix} = 60 s. Measurements are performed by a TGA-DSC system in the temperature range T = 25–700 °C at a heating rate r = 5 °C min⁻¹ and a synthetic air flow V = 25 mL min⁻¹. Catalyst-soot weight ratio is 4 : 1.

Conclusion

In this article, the characterization of co-precipitated CeO₂ and 1 : 1 mixed bismuth-ceria oxides by PXRD, Raman analysis, XRF, S_{BET}, and OSC_{dyn} and a comparison of different contact modes between catalyst and soot known in literature for the catalytic oxidation of soot by temperature programmed oxidation methods have been described. Additionally, an automated contact mode realized by an asymmetric dual centrifuge has been investigated.

According to PXRD and Raman analysis, the AdNanoCeria60 and the co-precipitated CeO₂ samples crystallize in the cubic fluorite-type CeO₂ structure without any oxygen defects, that is, without non-stoichiometry in the ceria lattice. The two parameters S_{BET} and OSC_{dyn} are very low for the co-precipitated CeO₂ samples. Therefore, the activity for soot oxidation is lower compared to the AdNanoCeria60 sample which has the highest S_{BET} = 60 m² g⁻¹ and OSC_{dyn} = 42 μmol O₂ g⁻¹ s⁻¹ and, consequently, the highest soot combustion activity of the catalysts investigated in this study. The results of PXRD and Raman analysis show that the BiCeO_{OA} samples consist of four crystalline phases, namely α- and β-Bi₂O₃, bismuthite Bi₂(CO₃)O₆, and a ceria phase with spatially inhomogeneous distribution of Bi³⁺ substitution for Ce⁴⁺ accompanied by oxygen lattice defects in the CeO₂ phase. The latter was modelled by two distinct CeO₂ phases in the Rietveld refinements with different site occupations factors sof(Bi²⁺). In contrast, the BiCeO_{AC} sample only reveals the Bi³⁺-doped CeO₂ phase together with a pure ceria phase and a small amount of bismuthite. The OSC_{dyn} of BiCeO₂_{AC} is, with ΔOSC_{dyn} = 19 μmol O₂ g⁻¹ s⁻¹, higher than that of BiCeO₂_{OA}. Therefore, BiCeO₂_{AC} has a higher activity for soot oxidation than BiCeO₂_{OA}. Additionally, the Raman spectroscopy data show that the mixed oxides have Frenkel defects. The intensity ratio I_{578}/I_{608}, which is proportional to the concentration of defects, is higher for the BiCeO₂_{AC} sample compared to the BiCeO₂_{OA} sample. Additionally, the particle size distribution measured by static light scattering is broad for the samples precipitated by AC with high availability of particles with hydrodynamic diameter below d_h = 10 μm. The particles in the samples precipitated by OA are more narrowly distributed with a maximum hydrodynamic diameter d_h = 11 μm. This could be the reason for the better OSC_{dyn} and the better activity. The mixed oxides reveal better soot combustion activities compared to their pure CeO₂ samples recognizable by the lower T_{50} values.

Regarding to the investigation of different contact modes between soot and catalyst for different catalysts, the loose and automated contact modes show good repeatability behavior. In marked contrast, tight and automated contact modes show good repeatability behavior. The automated contact has the advantage that there is no manual influence and is therefore not depending on the experimenter. Building on these results, the automated contact was further investigated. The rotation speed r and the mixing time t_{mix} were varied. The mixing time t_{mix} has a much lower effect on the T_{50} values than the rotation speed r.

Experimental Section

Catalyst Preparation

The chemicals listed below were used without further preparation. AdNanoCeria60 supplied by Evonik-Degussa with lot no. PH36701 and S BET = 60 m² g⁻¹ is used as reference material. All syntheses performed are described in detail in.[32]

Via co-precipitation, CeO₂ and the equimolar mixed oxide of cerium and bismuth are synthesized using the synthesis robot Accelerator SLT 106 from Chemspex Technologies AG, Switzerland. Two precipitants are used: 1 mol (NH₄)₂CO₃ (food grade, BASF, abbreviated as AC) and 0.6 mol C₂H₅OH·2 H₂O (99 %, ORG Laborchemie) dissolved in 1 L water (abbreviated as OA). The syntheses were performed in lined beakers with magnetic stirring bars. Using a thermostat from Huber Corp., the lined beakers were tempered to a temperature of T = 25 °C. The control of the thermostat was implemented in the “ApplicationExecutor” software for the syn-
thesis robot. For the co-precipitation, 0.5 mol Ce(NO$_3$)$_3$·6 H$_2$O and 0.5 mol Bi(NO$_3$)$_3$·5 H$_2$O (99.5%, Alfa Aesar) were dissolved in 1 L of 1 mol·L$^{-1}$ HNO$_3$ and transferred to beakers as reservoirs. With the help of the 4-needle head (4NH) of the synthesis robot, the volumes of the precursor solutions calculated were pipetted into lined beakers. For the mixed oxide Bi$_x$Ce$_{1-x}$O$_x$, abbreviated as BiCeO, equimolar amounts of the nitrate solutions are used. The precursors were mixed by magnetic stirring and kept at T = 25°C. In different lined beakers, the two precipitants, which were dissolved in ultra-pure water, were also brought to the temperature T = 25°C. The precipitants were transferred using the 4NH to the premixed and tempered nitrate solutions until the pH reached pH = 8 for AC and 3.5 times of the molar amount for OA was reached. The white to pale yellow precipitates were stirred for additional t = 0.5 h at T = 25°C. The precipitates were filtered off from the supernatants through a 3-fold parallel parallel filtration station at an over-pressure of $p = 1$ bar after stirring. For filtration, Polyethersulfone membranes (Sartorius Stedim Biotech Corp.) with 0.1 μm mean pore size were used. The filtered-off samples were dried overnight at room temperature, crushed and ground in an agate mortar until a fine powder was obtained and calcined at T = 800°C for t = 5 h.

Table 8. $T_{50}$ values of AdNanoCeria60 and BiCeO_OA measured at a TGA-DSC system in automated contact mode at different rotation speeds rs and mixing times $t_m = 60$ s and 300 s.

| rs [rpm] | T$_{50}$ ± $\sigma_{T_{50}}$ [°C] | T$_{50}$ ± $\sigma_{T_{50}}$ [°C] | T$_{50}$ ± $\sigma_{T_{50}}$ [°C] | T$_{50}$ ± $\sigma_{T_{50}}$ [°C] |
|----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 300      | 667.2 ± 2.0                     | 605.7 ± 0.2                     | 565.5 ± 0.4                     | 565.5 ± 3.4                     |
| 500      | 667.1 ± 1.8                     | 605.4 ± 1.6                     | 558.3 ± 3.6                     | 553.9 ± 1.3                     |
| 700      | 588.1 ± 1.5                     | 574.4 ± 1.6                     | 550.8 ± 0.1                     | 549.7 ± 1.1                     |
| 900      | 574.1 ± 1.6                     | 537.4 ± 0.9                     | 546.5 ± 1.6                     | 538.9 ± 3.5                     |
| 1100     | 545.3 ± 0.8                     | 520.1 ± 0.9                     | 534.7 ± 0.8                     | 536.5 ± 1.1                     |
| 1300     | 521.8 ± 0.7                     | 495.9 ± 1.8                     | 529.2 ± 0.7                     | 537.3 ± 0.9                     |
| 1500     | 518.8 ± 1.2                     | 476.2 ± 1.6                     | 530.4 ± 0.8                     | 535.0 ± 0.1                     |
| 1700     | 480.0 ± 1.3                     | 465.9 ± 1.0                     | 533.6 ± 1.0                     | 531.7 ± 1.3                     |
| 1900     | 457.0 ± 1.4                     | 437.1 ± 2.8                     | 529.5 ± 1.0                     | 527.1 ± 1.4                     |
| 2100     | 435.5 ± 1.2                     | 404.6 ± 0.7                     | 526.7 ± 0.6                     | 526.8 ± 1.2                     |
| 2300     | 416.3 ± 0.1                     | 399.3 ± 0.7                     | 526.4 ± 0.4                     | 523.4 ± 0.1                     |
| 2500     | 404.7 ± 1.3                     | 396.6 ± 1.0                     | 523.7 ± 0.1                     | 521.5 ± 1.3                     |
| 2700     | 402.8 ± 0.1                     | 395.6 ± 0.2                     | 524.0 ± 0.7                     | 520.6 ± 0.8                     |
| 2900     | 403.6 ± 0.1                     | 395.0 ± 0.1                     | 522.9 ± 1.5                     | 518.5 ± 0.1                     |
| 3100     | 393.9 ± 0.1                     | 396.6 ± 0.6                     | 520.4 ± 0.2                     | 516.8 ± 0.8                     |
| 3300     | 396.7 ± 0.1                     | 401.9 ± 1.0                     | 521.9 ± 1.9                     | 513.6 ± 0.7                     |
| 3500     | 402.9 ± 0.1                     | 405.3 ± 0.4                     | 523.5 ± 0.2                     | 514.2 ± 0.9                     |

Table 9 summarizes the dispensing and aspirating speeds of the 4NH.

**Contact between Soot and Catalyst**

A weight ratio of 4:1 of catalyst and soot is used for all tests. The model soot used in this work is the carbon black P90 supplied by Evonik Degussa.

Table 9. Dispensing and aspirating speed of the pipetting steps. The 4-needle head (4NH) of the synthesis robot Chemspeed Accelerator SLT106 is used for liquid dosing.

| Solution | Dispensing Speed [mL·min$^{-1}$] | Aspirating Speed [mL·min$^{-1}$] |
|----------|----------------------------------|----------------------------------|
| 0.5 mol·L$^{-1}$ Ce(NO$_3$)$_3$ | 40 | 40 |
| 0.5 mol·L$^{-1}$ Bi(NO$_3$)$_3$ | 40 | 40 |
| 1 mol·L$^{-1}$ (NH$_4$)$_2$CO$_3$ | 40 | 80 |
| 0.6 mol·L$^{-1}$ C$_3$H$_6$O$_2$ | 40 | 80 |
**Loose Contact**
Mixing soot and catalyst with a spatula for t = 60 s in a 5 mL glass vessel.

**Tight Contact**
Mixing soot and catalyst manually in an agate mortar for t = 300 s.

**Wet Contact**
Mixing soot and catalyst in acetone for t = 2.5 h in a 5 mL glass vessel under stirring. Afterwards, the suspension is dried for t = 48 h at T = 80 °C in order to get rid of acetone.

**Automated Contact**
The automated contact was performed using a dual asymmetric centrifuge Speedmixer™ DAC 150 from Hauschild Corp. Soot and catalyst are mixed in cups PPS–6 mL and the holder for a single sample was used. Experiments are performed at mixing times \( t_{mix} = 60 \text{s} \) and 300 s. The rotation speed \( r_s \) is varied in \( \Delta r_s = 200 \text{ rpm} \) steps between \( r_s = 300 \) and 3500 rpm.

**Activity Measurements**
The activity measurements in means of \( T_{ad} \) values and dynamic oxygen storage capacity \( OSC_{dyn} \) were investigated by automated serial thermogravimetric analyses coupled with heat flow differential scanning calorimetry (TGA-DSC 1 1600 from Mettler Toledo Corp.) according to Ref. [32]. Catalysts calcined at \( T = 800 \text{ °C} \) were used for activity measurements. The \( T_{ad} \) value is the temperature where 50% of the soot mass is oxidized. To determine the \( T_{ad} \) values, approximately \( m = 10 \text{ mg} \) of the catalyst-soot mixture in a 4:1 weight-ratio was placed in a corundum crucible of volume \( V = 70 \text{ µL} \) and heated to a temperature of \( T = 700 \text{ °C} \) at a heating rate of \( r = 5 \text{ °C.min}^{-1} \) with a synthetic air flow rate of \( V = 25 \text{ mL.min}^{-1} \). The \( T_{ad} \) values were determined using the software Star™ (Mettler Toledo Corp.).

The dynamic oxygen storage capacity \( OSC_{dyn} \) is another significant property for soot oxidation catalysts. The \( OSC_{dyn} \) was determined experimentally with the TGA-DSC 1 1600 from Mettler Toledo Corp. already described. Two heating and cooling cycles were performed in order to calculate the \( OSC_{dyn} \). Approximately \( m = 30 \text{ mg} \) of the catalyst was placed in a \( V = 70 \text{ µL} \) corundum crucible and heated to \( T = 700 \text{ °C} \) under nitrogen flow of \( V = 25 \text{ mL.min}^{-1} \) to get rid of adsorbed oxygen, water, or other compounds. The system was stabilized for \( t = 10 \text{ min} \). Afterwards, the system was cooled to \( T = 150 \text{ °C} \) under synthetic air flow of \( V = 25 \text{ mL.min}^{-1} \) for oxygen uptake and then stabilized for \( t = 10 \text{ min} \). This procedure was repeated and the weight loss of the second heating step was used for calculating the \( OSC_{dyn} \) as mass difference of \( \Delta m_{ad} = m_{ad}-m_{cat} \).

The formula symbols have the following meaning: \( m_{ad}^{100} \text{ °C} \) is the mass of catalyst at a temperature of \( T = 150 \text{ °C} \) after oxygen uptake, \( m_{cat}^{700} \text{ °C} \) is the mass of catalyst at \( T = 700 \text{ °C} \) after oxygen release, \( m_{oxy} \) is the molar mass of oxygen, and \( m_{cat} \) is the buoyancy-corrected mass catalyst weighed in a \( V = 70 \text{ µL} \) corundum crucible after desorption of compounds such as water. \( OSC_{dyn} \) is given in \( \mu \text{mol. g}^{-1} \). The heating/cooling rate of \( r = 5 \text{ °C.min}^{-1} \) was used for TGA-DSC measurements.

**Catalyst Characterization**
Powder X-ray diffraction (PXRD) was performed on a Bruker D8 diffractometer with Co fine focus X-ray source (Ni filter, \( \lambda_{Co} = 1.79021 \text{ Å}, \Theta–\Theta \) geometry, VDS, Lynxeye detector) for the co-precipitated samples. For the reference sample AdNanoCeria, the diffractometer STOE-Stadi P with Cu fine focus X-ray source (monochromator, \( \lambda_{Cu} = 1.54056 \text{ Å}, \Theta–\Theta \) geometry, MYTHEN2 R1 K detector) was used. The intensity data were collected in the 2θ range from 20–125°. Qualitative phase identification was evaluated by diffraction pattern assignment according to ICDD (International Centre for Diffraction Data) data as specified. Crystalline phases were identified through Rietveld refinement using the software TOPAS version 4.2 according to Refs. [45–47], which was adapted for the cerium-bismuth mixed oxides. Instrumental parameters for the fundamental parameter TOPAS refinement have been determined by refining a LaB\(_6\) diffraction pattern as reference sample. Raman spectra were measured with an inVia Raman Microscope (Renishaw Corp.). A frequency-doubled Nd\textsubscript{3}YAG laser of the model RL473 C from Renishaw with a wavelength of \( \lambda = 532 \text{ nm} \) and a UVDD-CCD-Array detector with a grid consisting of 1800 lines/mm was used. Normally, laser powers of 0.5% of the maximal laser power \( P = 50 \text{ mW} \) and a measuring time of \( t = 60 \text{ s} \) were employed. The calcined samples were placed on a 96-well microplate with V-shaped bottom (Greiner Corp.). The operating status of the microscope was line focus. Each sample was measured at three different points.

The determination of the specific surface according to Brunauer, Emmett and Teller was measured on a NOVA touch LX4 surface area & pore size analyzer (Quantachrome Corp.). The evaluation was performed with the software TouchWin™ version 1.11 (Quantachrome Corp.). The specific surface was measured by \( N_2 \) adsorption-desorption isotherms at the temperature of liquid \( N_2 \) with \( T = -196 \text{ °C} \). In preparation for the measurements, the samples were degassed under high vacuum for \( t = 4 \text{ h} \) at \( T = 250 \text{ °C} \). The seven-point multi-point BET method was used to determine the specific surface \( S_{ BET} \) in a relative pressure range of 0.02–0.25.

To determine the mass fractions of Bi and Ce, Energy-dispersive X-ray fluorescence (XRF) analyses were performed on a Fischerscope® X-RAY XAN® instrument and the evaluations with the software WinFTM® (Fischer Corp.). For the measurements, an excitation voltage of \( U = 30 \text{ keV} \) and a measuring time of \( t = 60 \text{ s} \) were used. The calcined catalysts were placed on a cellulose foil. Three repeated measurements were made at different locations on the sample and the composition average was taken. Calibration of the measurement data was performed using a standardless fundamental parameter method supplied by Fischer Corp. More details are described in Refs. [48–51].

Particle size distribution was measured by static light scattering performed on a CILAS 930 particle size analyzer. The range of hydrodynamic diameter was between \( d_h = 0.2–500 \mu \text{m} \). Approximately \( m = 0.5 \text{ g} \) of the catalysts were suspended in the water container of the analyzer at \( T = 25 \text{ °C} \) and ambient pressure. In preparation of the particle size measurement, the samples dispersed in water were treated with ultrasound for \( t = 60 \text{ s} \) to destroy agglomerates. This procedure was repeated for five times.

**Author Contribution**
S. C. H. built the experimental setups, performed experiments, analyzed data, and wrote this paper. K. S. supervised the work.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: automated catalyst soot contact · automated co-precipitation · catalyst soot contact · cerium-bismuth oxides · diesel soot oxidation

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