Perovskite Catalyst for In-Cylinder Coating to Reduce Raw Pollutant Emissions of Internal Combustion Engines

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ABSTRACT: Aiming to achieve the highest combustion efficiency and less pollutant emission, a catalytic coating for cylinder walls in internal combustion engines was developed and tested under several conditions. The coating consists of a La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3} (LSCO) catalyst on an aluminum-based ceramic support. Atomic force microscopy was applied to investigate the surface roughness of the LSCO coating, while \textit{in situ} diffuse infrared Fourier transform spectroscopy was used to obtain the molecular understanding of adsorption and conversion. In addition, the influence of LSCO-coated substrates on the flame quenching distance was studied in a constant-volume combustion chamber. Investigations conclude that an LSCO coating leads to a reduction of flame quenching at low wall temperatures but a negligible effect at high temperatures. Finally, the influence of LSCO coatings on the in-cylinder wall-near gas composition was investigated using a fast gas sampling methodology with sample durations below 1 ms. Ion molecule reaction mass spectrometry and Fourier transform infrared spectroscopy revealed a significant reduction of hydrocarbons and carbon monoxide when LSCO coating was applied.

1. INTRODUCTION

Achieving the highest combustion efficiency is one of the fundamental objectives in the development of modern internal combustion engines. To achieve this goal, new combustion processes are being developed that are based on highly diluted fuel/air mixtures in the combustion chamber. In such cases, the increase of the flame quenching distance at the combustion chamber walls has a negative effect on the overall process efficiency and raw pollutant emissions. In-cylinder catalytic coatings aim for a higher reactivity of the near-wall gases, resulting in a reduced flame quenching thickness and lower hydrocarbon and carbon monoxide concentrations. It has already been shown that such coatings are suited to reduce the burning delay, increase combustion speed, and improve the overall efficiency without compromising stability.\textsuperscript{2–5} For example, Hultqvist et al. first reported the impact of thermal and catalytic coatings on unburned hydrocarbons in a homogeneous charge compression ignition engine.\textsuperscript{6} They concluded that a thin thermal barrier coating (150 μm) reduces unburned hydrocarbon emissions, while a thick thermal barrier (600 μm) or platinum-doped catalytic coating increases the emission of unburned hydrocarbons. Osipov et al. investigated the CO conversion of different coatings within a flow reactor. In their study, a palladium-based catalyst with an Al–Si alloy surface showed the highest catalytic activity with a 50% conversion at 152 °C.\textsuperscript{7}

While these investigations have been performed using conventional fuels, the concept of catalytic coatings requires further investigations, when novel renewable fuels, such as e-fuels or biohybrid fuels, will be applied since they enable significantly lower reaction temperatures.\textsuperscript{8} The most common catalyst compounds, which facilitate the oxidative conversion of unburned fuel components, are typically based on precious metals deposited on thermally stable oxides, such as stabilized ZrO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}. These oxides then act as thermal barriers and normally require a two-step deposition process that increases the cost of application significantly.\textsuperscript{9–12} With respect to the specific requirements that arise from next-generation fuels, in particular, low combustion temperatures,\textsuperscript{13} new catalytic coatings are highly desirable that exhibit low light-off temperatures, noble-metal-free materials, as well as a single processing step.

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Perovskite-type oxides (ABX$_3$) are promising alternatives for precious-metal oxidation catalysts in various catalytic applications thanks to their low cost, high hydrothermal stability, and poisoning resistance.\textsuperscript{14–16} Perovskites that contain a lanthanide element at position A and a transition metal at position B are used more frequently in heterogeneous catalysis because of their structural features. They could accommodate around 90% of the metallic natural elements of the Periodic Table that stand solely or partially at the A and/or B positions without destroying the matrix structure, offering a way of correlating compositional to catalytic features.\textsuperscript{17,18} In many applications, perovskites have shown excellent catalytic properties, including photocatalysis in NO reduction/oxidation,\textsuperscript{19} and CO oxidation.\textsuperscript{20} Nevertheless, they are still rarely used in practice. To the best of our knowledge, perovskite oxides have not been reported to act as a catalytic coating in engines.

In this work, La$_{0.8}$Sr$_{0.2}$CoO$_3$ (LSCO) was selected as a model catalyst for the investigation of low-temperature CO conversion since LSCO has already been proven as a Mars–van-Krevelen-type oxidation catalyst. To study the fuel–catalyst interactions under model conditions, LSCO powder was deposited onto alumina-based ceramic chips as a catalytic coating. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were conducted to investigate the coating parameters and quality. With the LSCO powder as the reference, \textit{in situ} diffuse infrared Fourier transform spectroscopy was employed to compare the chemical adsorption mechanism during the CO oxidation. To evaluate the influence of LSCO coatings on the flame quenching distance, a quenching object made of AlMg$\textsubscript{1}$ (EN AW-5005) was coated with LSCO and studied in a constant-volume combustion chamber. Eventually, the influence of LSCO coatings on the in-cylinder wall-near gas composition was investigated using a fast gas sampling methodology. The valve was flush-mounted into a single-cylinder engine with an adapter, whose surface was coated with LSCO. The samples that were taken above the coated adapter were then diluted by a transport gas and further analyzed with ion molecule reaction mass spectroscopy (IMRMS) and Fourier transform infrared (FTIR) spectroscopy.

2. RESULTS AND DISCUSSION

\subsection*{2.1. Fundamental Investigation}

\subsection*{2.1.1. Particle Structural Properties.} As illustrated in Figure 1, La$_{0.8}$Sr$_{0.2}$CoO$_3$ belongs to the general perovskite formula of ABO$_3$. Co ions are coordinated with six oxide ions, and the CoO$_6$ units are connected by the corner-sharing manner, forming networks in which La/Sr ions are located in the dodecahedral site of framework. Transition-metal Co ions have high oxidation ability toward CO, and the substitution of La$^{3+}$ ions by Sr$^{2+}$ ions gives rise to the increase in the oxidation state of Co$^{3+}$ to Co$^{4+}$, which improves the oxidizing ability of the oxides.\textsuperscript{21} However, according to a recent X-band continuous-wave electron paramagnetic resonance (EPR) investigation, a negligible amount of Co$^{4+}$ is formed when 20% La$^{3+}$ is substituted by Sr$^{2+}$ in perovskites.\textsuperscript{22} This indicates the existence of anion defects in crystal structure so that in La$_{0.8}$Sr$_{0.2}$CoO$_3$, oxygen vacancies are present to maintain the charge neutrality.

The particle size of LSCO was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Figure 2a,b. The particles possess a random shape and distribute homogeneously with the average size ranging from 50 to 300 nm. In the TEM image, small particles with diameters of less than 10 nm can be observed. Nevertheless, small particles tend to agglomerate together, which is a common phenomenon for nanoscale materials.\textsuperscript{23} Moreover, N$_2$ adsorption/desorption measurement was conducted to investigate the particle surface area. Figure 2c displays the isotherms with the Brunauer–Emmett–Teller (BET) area of 13.8 m$^2$ g$^{-1}$, which is larger than many reported LSCO perovskites\textsuperscript{24,25,28} as shown in Figure 2d. The relatively large specific surface area is conducive to expose more oxygen vacancies,\textsuperscript{26} which plays an important role in the process of CO oxidation.

\subsection*{2.1.2. CO Conversion.} To clarify the catalytic activity of LSCO powder, CO was chosen as the species for the conversion test. The CO conversion of LSCO powder is shown in Figure 3. The light-off temperature, i.e., the temperature at which CO conversion reaches 50%, is 125 $^\circ$C, while the temperature of 90% conversion is 155 $^\circ$C. The catalytic activity is comparable to or even better than the majority of reported perovskite powder catalysts.\textsuperscript{31} The good CO conversion performance could be attributed to the large specific surface area, which increased the amount of surface oxygen vacancy, thus enhancing the adsorption process of O$_2$ molecules.\textsuperscript{31,32} To further investigate the resistance of the LSCO catalyst toward deactivation, a long-term stability test at 160 $^\circ$C for 40 h has been performed (see Figure 3b). With a constant gas atmosphere, the CO conversion decreases from 93 to 86% after reaction for 2 days, which is considerable for a nanosize catalyst. The acceptable deactivation indicates the good stability of LSCO toward CO oxidation.

\subsection*{2.1.3. In Situ DRIFTS.} To study both the adsorption and conversion of CO and other intermediates and products under reaction conditions, \textit{in situ} DRIFTS was employed. First, the LSCO powder was placed inside a high-temperature pretreated reaction chamber. Then, a gas flow of 0.5% CO + 10% O$_2$ was fed onto the catalyst and held for 30 min at 50, 150, and 250 $^\circ$C, respectively. The spectra collected at these temperatures are shown in Figure 4a. The rotational–vibrational CO bands are observed at 2113 cm$^{-1}$ (center of P-branch) and 2173 cm$^{-1}$ (center of R-branch), attributed to the co-adsorption of the gas-phase and linearly adsorbed CO on the LSCO surface.\textsuperscript{27} Due to the overlapping peak positions, to identify the adsorbed CO in the presence of gas-phase CO, \textit{in situ} DRIFTS was conducted after flushing the catalyst with a gas...
flow of pure N2 for 30 min. As seen in Figure 4b, the intensities of the two bands become weaker compared with those in the atmosphere in CO, which indicates that the observed bands at ~2150 cm⁻¹ in Figure 4a can be assigned to CO gas as well as the adsorbed CO. When the temperature increases to 150 °C, two peaks at 2337 and 2358 cm⁻¹ increasingly appear that are assigned to CO₂ in the gas phase, indicating the oxidation of CO toward CO₂ at 150 °C. A stronger CO₂ band and a weaker CO band can be observed at 250 °C, which is consistent with an enhanced oxidation of CO at a high temperature. The
The decrease of CO band indicates that the gas-phase CO dominates the peaks at 2113 and 2173 cm\(^{-1}\). Meanwhile, the peaks of bidentate carbonate intermediate species appeared in the range of 1450 to 1600 cm\(^{-1}\), showing in a gray shaded area, suggesting that the CO oxidation route on the LSCO surface evolved from bidentate carbonates to uncoordinated carbonate ions and finally to CO\(_2\).3333

2.1.4. Coating Characterization. SEM was used to show the details of the LSCO coating on a ceramic substrate. The top-view SEM image in Figure 5a shows that the LSCO coating resulted in a homogeneous distribution of the deposit due to the small particles of the LSCO powder. The film coating did not change the morphology or state of the LSCO powder. Solely, the powder distribution became denser on the substrate. As shown in Figure 5b, the LSCO drop coating formed as a roughly 50 \(\mu\)m thick film on the surface of the ceramic substrate. The study of the surface topography of the coated substrate was carried out using AFM. Figure 5c,d shows the contact mode of the LSCO film as two-dimensional (2D) and three-dimensional (3D) AFM topographic images. Some convex and concave spots were found in the 2D topographic image. The highest difference on the surface of the coated LSCO is up to \(\sim 3 \mu m\) since no further compaction action was taken after the coating procedure. Compared with radio-frequency magnetron sputtering technique, the coated substrate has a large surface roughness, which affects the velocity field, thus providing a highly accessible surface for the gas diffusion and adsorption.35

To study the dynamic nature of the gas adsorption behavior in CO conversion for the LSCO powder and the coated substrate, in situ DRIFTS was conducted. Figure 6 shows the result of CO adsorption and oxidation at 150 °C, which is higher than the light-off temperature. The spectra indicate that the CO reaction behavior of the film-coated substrate is similar to that of LSCO powder in the wavenumber range above 2000 cm\(^{-1}\). It is most likely due to the thick film deposition, which behaves like a bulk sample. Linearly adsorbed and gas-phase CO bands at 2113 and 2173 cm\(^{-1}\) are present, while no bridged CO adsorption band was observed.24,36 According to the CO conversion result in Figure 6a, the reaction temperature is higher than the light-off temperature, which indicates that a certain amount of CO\(_2\) has been produced. Consequently, two gas-phase CO\(_2\) peaks at 2337 and 2358 cm\(^{-1}\) appeared. Additionally, the peaks of bidentate carbonate intermediate species, appearing in the range of 1450–1600 cm\(^{-1}\), are only detectable in the powder sample. This suggests that the CO oxidation route for LSCO powder is from adsorbed CO to bidentate carbonate and eventually to CO\(_2\), while the CO was directly oxidized to CO\(_2\) without significant
(or detectable) amounts of intermediate species on the surface of the film-coated sample.\textsuperscript{24} We tentatively assume that the coating procedure has affected the surface states of LSCO in terms of porosity and oxygen defect concentration, which then may change the CO oxidation pathway.

2.2. Investigations under Engine Relevant Conditions. 2.2.1. Impact on Quenching Distance. A large amount of unburned hydrocarbons emitted from an engine results from the fact that flame cannot reach certain engine geometries and extinguishes in narrow crevices.\textsuperscript{37} This is caused by heat losses from the flame to colder cylinder walls, which extinguish the flame at a characteristic distance, the quenching distance.\textsuperscript{38} Since this distance mainly determines whether a flame can enter a crevice, it is an important parameter for the emission of unburned hydrocarbons.

Figure 7a shows the quenching distances of uncoated (black) and LSCO-coated (red) AlMg1 quenching objects. The gas and wall temperatures were set to 27 °C (closed symbols) and 163 °C (open symbols). In addition, as in the study of Karrer et al.,\textsuperscript{39} least-squares compensation curves of the form $d_q = k'p^n$ were derived from the measured values and displayed as lines in the diagram. Solid lines represent the fit for a temperature of 27 °C, and dashed lines represent the fit for a temperature of 163 °C. Due to the uncertainty in the position determination based on the resolution, error bars of ±10.4 μm are depicted. The calculated compensation curves are within the error limits of all experimental values. The decreasing effect of quenching distance with increasing pressure is clearly visible\textsuperscript{40} as well as the decreasing effect of temperature.\textsuperscript{41} Nevertheless, the impact of temperature change is more pronounced for the uncoated wall.

For better comparability, in Figure 7b, the experimental values were normalized using the Péclet number, similar to the work of Haber et al.\textsuperscript{41} The Péclet number is defined as the ratio of quenching distance to the theoretical flame thickness. Flame thicknesses were determined by $d_f = k/(\rho c_p s_i n)$. The necessary parameters were calculated using the Cantera software package\textsuperscript{42} and the NUIGMECH1.1.\textsuperscript{43} For a constant temperature, the Péclet number of a quenching object is approximately constant.\textsuperscript{40} At low wall temperatures, the uncoated quenching object has a Péclet number of 6.2 and the coated one has a Péclet number of 5.4. In this case, the LSCO could act as a thermal barrier since it quickly adapts to the gas temperature due to the high porosity and therefore low volumetric heat capacity but does not transfer the heat to the aluminum substrate because of its low thermal conductivity. This leads to a decreased heat loss, which in turn leads to a smaller quenching distance/Péclet number.\textsuperscript{6} In the current study, it could not be tested whether the catalyst heats up sufficiently at such low temperatures to be catalytically active.

At a higher temperature of 163 °C, the Péclet number of aluminum decreases by 1.2, while the Péclet number of the LSCO-coated aluminum only decreases by 0.5. There are two
observed that the unburned fuel hydrocarbons (C₂H₅OH, = 1.7) engine operation with the uncoated adapter, it can be = 12 bar. Comparing stoichiometric (AFR = 1) and lean (AFR and the resulting indicated mean e

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possible explanations: (1) adsorption of the reactive radicals from the preheating zone on the surface as observed in other studies, for different catalytic materials and (2) a reduction of the thermal barrier effect of the LSCO since the overall heat losses are reduced at higher wall temperatures. The possibility of partial fuel conversion by the catalyst at low gas temperatures of 163 °C even before the experiment starts is less probable because Yang et al. reported the initiation of propane conversion to happen at temperatures of 200 °C for LSCO. Regardless of the smaller change in quenching distance, the coated aluminum still has a smaller Péclet number than the uncoated aluminum. In a follow-up study, inert perovskite coatings and gas sampling could be used to differentiate the influence of thermal and catalytic coating properties.

2.2.2. Influence on the In-Cylinder Near-Wall Gas Composition in a Spark-Ignited (SI) Engine. Future spark-ignited internal combustion engines, aiming for ultrahigh efficiencies above 50% and low raw pollutant emissions, will be operated with relative air/fuel ratios (AFR) >1. However, ultraclean engine operation leads to increased flame quenching distances due to the colder combustion, which in turn leads to increased hydrocarbons and carbon monoxide emissions.

Here, LSCO was applied to the surface of the adapter facing the combustion chamber using the aforementioned drop coating method. The engine speed was set to \( n = 2500 \text{ min}^{-1} \) and the resulting indicated mean effective pressure was IMEP = 12 bar. Comparing stoichiometric (AFR = 1) and lean (AFR = 1.7) engine operation with the uncoated adapter, it can be observed that the unburned fuel hydrocarbons (C₂H₅OH, C₆H₁₂, C₆H₁₀) significantly increase at lean engine operation, while the intermediate hydrocarbon species (C₄H₂, C₅H₁₀) and carbon monoxide (CO) decrease with lean engine operation. This can also be observed for the raw emissions of an SI engine. By applying an LSCO layer of 60 μm to the valve adapter, a significant reduction of the hydrocarbons and carbon monoxide can be observed for lean and stoichiometric operation (see Figure 8).

Applying the derived measurement error suggests that the fuel hydrocarbons can be significantly reduced with the coating under both stoichiometric and lean conditions. Carbon monoxide can also be significantly reduced under stoichiometric conditions and shows only little reduction under lean conditions since carbon monoxide emissions are already reduced by the excess air of the lean engine operation. The applied fast gas sampling method does not allow us to assess whether the reduction in hydrocarbons near the wall is due to a reduced flame quenching distance or a postcombustion catalytic conversion. Therefore, the impact of these effects must be further investigated.

After the engine tests, the coated adapter was inspected again. It is important to note that despite the subsequent calcination treatment, the film coating is not robust enough to persist under a harsh combustion condition. The coated LSCO on the cylinder adapter was slightly removed. To obtain robust and optimized catalytic coating, the radio frequency (RF) sputtering technique was employed to deposit LSCO on alumina-based ceramic substrates for a preliminary test. The results show that sputtering leads to a homogeneous coating layer, but the low surface roughness of sputtered LSCO prohibits the extensive CO adsorption.

3. CONCLUSIONS

To better understand the interactions between the fuel and the catalytically coated combustion chamber walls of an SI internal combustion engine, the LSCO catalyst was deposited on an alumina-based ceramic substrate. The film coating results in a large roughness, which is accessible for gas adsorption. By in situ DRIFTS measurements, the CO adsorption and oxidation behavior was investigated. The results showed that LSCO has a low light-off temperature of 123 °C and that there is a different fuel conversion pathway between the LSCO particles and the LSCO coating. Also, it is found that the film coating leads to a thick layer and high mass loading of LSCO but forms unstable coatings. Film coating was used for tests in a constant-volume combustion chamber and with a gasoline engine to analyze the catalytic effect on pollutant emissions. During the combustion tests, it was found that the flame quenching distance at low wall temperatures was reduced when the LSCO coating was applied to the AlMg1 object; meanwhile, the impact was negligible for high wall temperatures. The effect of the LSCO coating on the composition of gases near cylinder wall in the fired engine was investigated using a fast gas sampling method. A significant reduction in hydrocarbons and carbon monoxide was found when the LSCO-coated adapter was used. If the LSCO coating is applied by the sputtering method, a robust but very thin coating is produced, which initially showed a lower oxidation effect in initial studies. To present a further optimized catalytic coating, suspension plasma spraying will be used for further investigations in our work.

4. EXPERIMENTAL SECTION

4.1. Characterization. La₀.₈Sr₀.₂CoO₃ (LSCO) was purchased from Sigma-Aldrich and was used as received.

Scanning electron microscopy (SEM) measurements were carried out using a LEO/ZEISS Supra 35 VP microscope equipped with a Gemini column and a field emission gun. Bright-field transmission electron microscopy (TEM) images were recorded with a ZEISS LIBRA 200 FE microscope operating at 200 kV. The multipoint Brunauer–Emmett–Teller (BET) surface area was obtained with a Micromeritics ASAP 2060 Instrument (Micromeritics) by measuring the nitrogen physisorption at a temperature of 77 K after degassing (0.4 kPa total pressure at 523 K for 4 h). Atomic force microscopy (AFM) was performed with the NanoWizard NanoOptics and Vortex2 SPMControl station by Bruker Nano GmbH and JPK BioAFM. Topographic images were acquired in intermittent contact mode (AC mode) using an OTESPA probe (OPUS by MikroMasch) purchased from Nano-AndMore GmbH with a nominal resonance frequency of 300 kHz in air, a nominal spring constant of 26 N/m of the cantilever, and a tip radius of <7 nm. The calibration of the cantilever was conducted contactless. AC mode measurements were performed with a scan size of 50 × 50 μm² and 512 × 512 pixels.

4.2. Catalytic Activity. Around 100 mg of LSCO powder was loaded into a quartz tube reactor with a diameter of 1 cm and fixed with quartz wool. For pretreatment, the tube reactor with the LSCO catalyst was heated in O₂ up to 300 °C at a ramping rate of 7.5 °C min⁻¹ in a vertical tube furnace (RS232, HTM Reetz GmbH) and then held at constant temperature for 1 h. When the reactor and the furnace were cooled down to 50
3°C after pretreatment, the gas feed was changed to a mixture of CO/O₂/N₂ (0.5% CO, 10% O₂, and balance N₂, total 100 mL min⁻¹) to study the CO oxidation. The initial measurement at 40 °C was kept for 4 h. Then, the temperature was increased and held for 2 h every 20 °C up to 220 °C. The outlet gas composition was analyzed by an FTIR gas analyzer (Model 2030, MKS INSTRUMENTS). The CO conversion was calculated based on eq 1

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\text{CO conversion (\%) } = \frac{C_{\text{inlet,CO}} - C_{\text{outlet,CO}}}{C_{\text{inlet,CO}}} \times 100%
\]

where \(C_{\text{inlet,CO}}\) and \(C_{\text{outlet,CO}}\) are the CO concentrations corresponding to the inlet and outlet of the reactor, respectively.

4.3. Coating. Aluminum oxide chips equipped with a back-side resistive heating circuit (99.6% aluminum oxide, Universität Bayreuth, Bayreuth, Germany) were used as substrates to deposit the LSCO catalyst, which has been reported by our previous work.33–35

For the coating process, 10 mg of LSCO powder was dispersed into a 0.5 mL absolute ethanol solvent and a slurry of 20 mg mL⁻¹ LSCO suspension was formed by applying ultrasonication for 30 min to ensure a proper homogenization. Then, the substrate was fixed in a homemade Teflon mask and the mentioned suspension was deposited dropwise on the ceramic substrate. This process has been combined with a drying procedure at 50 °C after each drop to remove the solvent. Finally, the coated substrate was heated at 500 °C for 4 h in air to ensure a stable deposition. To coat the quenching object and valve adapter, the surfaces were cleaned with ethanol and the LSCO suspension was applied with the described procedure.

4.4. In Situ DRIFTS. The LSCO powder (approx. 100 mg) was placed inside a high-temperature reaction chamber (HVC–DRP, Harrick Scientific Products, Inc.) for in situ DRIFTS measurements. Infrared spectroscopy in diffuse reflection mode was applied using an FT-IR VERTEX 70 device (Bruker) and a Harrick Praying Mantis mirror system. The LSCO catalyst was heated to 300 °C and held at that temperature for 1 h in an O₂ stream (with a flow rate of 100 mL min⁻¹) for the pretreatment. After that, the gas feed was changed to N₂ and the chamber with the catalyst was cooled down and kept at 250, 150, and 50°C. The spectrum of N₂ was recorded as background and subtracted from the spectra collected afterward. A flow of 0.5% CO, 10% O₂, and balance N₂ (total, 100 mL min⁻¹) was fed onto the catalyst surface and held for 30 min, and the spectra were collected simultaneously.

4.5. Constant-Volume Combustion Chamber. For the flame investigations, the aforementioned LSCO was drop-coated to a cuboid AlMg₁ object that was installed into a constant-volume reactor (see Figure 10a). The stainless steel reactor has a volume of approximately 500 mL with a design pressure of 40 bar and an optical access made of fused silica. Additionally, the reactor is equipped with a controlled heating system and a gas manifold for the mixture preparation. This mixture preparation is based on the partial pressure method, and the pressure is measured by two static pressure sensors (STS PTM/RS485, 500 mbar and 5 bar). During the experiment, the dynamic pressure rise is recorded with a Kistler 6125C11U20. The quenching object has a size of 5.5 × 5.5 × 16 mm³. Through SEM measurements, the coating thickness was determined to be approximately 40 μm. The experimental setup is based on the work of Karrer et al.39 A fuel-rich (φ = 1.2) propane–air mixture is spark-ignited, causing a flame that propagates parallel to the surface of the quenching object. With a flame-wall interaction length of approximately 6 mm, an image in the visible light spectrum is taken by an ORCA-Spark CMOS camera. The image has a resolution of 5.2 μm/pixel and an exposure time of 126 μs. Then, an OpenCV-based processing code56 extracts the flame front and quenching object contours. Afterward, the respective minimum distance is calculated (see Figure 10b). The criterion for identifying the outer flame front was 60% of the maximum intensity since this value resulted in the smallest scattering of the derived quenching distances. Then, the quenching distances of the left and right sides were averaged. The initial pressure was varied from 0.6 to 1.2 bar, but due to combustion, the pressure at which the image was taken was slightly higher (<20%). Besides, the wall and gas temperatures were set to 27 or 163 °C, respectively.

4.6. Fast Gas Sampling Methodology. The fast gas sampling valve (Kistler Instruments GmbH) enables sampling durations of less than 1 ms. The sampling duration is adjusted by the stroke of the valve. After sampling, the sample is mixed with nitrogen as a transport gas in a mixing chamber. A heated line to the analyzers is used to avoid condensation. Next, Fourier transform infrared (FTIR) spectroscopy and fast ion molecule reaction mass spectrometry (IMR-MS) allow the determination of the sample composition over a specified sampling time. Since the analyzers require a certain volumetric gas flow, the transport gas flow is adjusted to the minimum necessary value to reduce the dilution of the sample as much as
possible. The outward opening sampling valve is actuated with a tappet by an electromagnet. Depending on the valve temperature, wear can occur at the contact between the valve and tappet, which limits the possible measuring cycles. Also, the contact surface between the valve and valve seat is susceptible to wear caused by combustion particles. The lack of lubrication leads to wear, which can lead to leakage with increasing measurement cycles. To eliminate such leaks, the valve must be periodically reground.

Figure 11 shows the application of the fast sampling valve to the engine. Valve (3) is positioned inside the cylinder head of the single-cylinder engine between intake (1) and exhaust valve (6) using an adapter (4), whose surface facing the combustion chamber can be coated. The surface to be coated as an area of \(A_{\text{adapter}} = 87.464\ \text{mm}^2\). As it can be seen from the CAD data, the valve is not flat with the combustion chamber due to available space for the application of the valve. The single-cylinder engine features a swept volume of \(V = 500\ \text{cm}^3\), a stroke-to-bore ratio of 1.5, and a compression ratio of \(CR = 10.8\). Further, the fuel (RON95E10) was injected by a central direct injection (2) with an injection pressure of \(p_{\text{Fuel}} = 200\ \text{bar}\). The injection was conducted at SOI (start of injection) = 300° CA (crank angle) before firing top dead center, which leads to a homogeneous fuel–air mixture at ignition by the spark plug (5). The relative air–fuel ratio was set to stoichiometric conditions \(\lambda = 1.0\).

To assess the effects of coatings on the reduction of unburned hydrocarbons and carbon monoxide, the uncertainty of the measurement system was evaluated. Since the combustion process is subject to cyclic variations, the evaluation of only a few individual measurements is not meaningful. Therefore, an average is derived from the evaluation of four different operating conditions, which were repeatedly (8 times for each operating condition) and nonconsecutive adjusted. One measurement consists of 25 samples every 50 engine cycles. By considering the mean value and standard deviation of these measurements for each species, a measurement error for the measurement setup can be determined, which is then applied to the measured concentrations.

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Notes
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