Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence

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Visualizing and measuring the gas distribution in close proximity to a working catalyst is crucial for understanding how the catalytic activity depends on the structure of the catalyst. However, existing methods are not able to fully determine the gas distribution during a catalytic process. Here we report on how the distribution of a gas during a catalytic reaction can be imaged in situ with high spatial (400 μm) and temporal (15 μs) resolution using infrared planar laser-induced fluorescence. The technique is demonstrated by monitoring, in real-time, the distribution of carbon dioxide during catalytic oxidation of carbon monoxide above powder catalysts. Furthermore, we demonstrate the versatility and potential of the technique in catalysis research by providing a proof-of-principle demonstration of how the activity of several catalysts can be measured simultaneously, either in the same reactor chamber, or in parallel, in different reactor tubes.
Catalysis research is highly relevant to society because industrial production of chemicals and environmental protection by pollution control rely heavily on (heterogeneous) catalyst technologies. In this context the oxidation of carbon monoxide (CO) on Pt-group metals is one of the most-studied prototypical catalytic reactions because of its practical relevance and general applicability. Despite its apparent simplicity, the reaction is challenging to study and describe because of peculiar kinetics such as bistability and oscillations, and fascinating spatiotemporal behaviour.

In the case of industrial catalyst development, the efficiency of a material to catalyse a particular reaction is evaluated by analysing the end products, after the reactants have passed the catalyst containing the active material, using appropriate characterization techniques, such as mass spectrometry (MS), gas chromatography (GC), Fourier transform infrared spectroscopy (FTIR) or specific analysers depending on the reaction. However, for model catalysts, such as single crystals, used to yield geneous) catalyst technologies. In this context the oxidation of carbon monoxide (CO) on Pt-group metals is one of the most-studied prototypical catalytic reactions because of its practical relevance and general applicability. Despite its apparent simplicity, the reaction is challenging to study and describe because of peculiar kinetics such as bistability and oscillations, and fascinating spatiotemporal behaviour.

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Nonintrusive laser-based techniques, such as Laser-induced fluorescence (LIF) have been used in numerous research fields, such as combustion and medical research, to measure temperature, velocity and the concentration of a probed gas. LIF has high spatial and temporal resolution, is nonintrusive and can be used to perform 2D measurements in situ without disturbing the flow properties of the gas. It is then often referred to as planar laser-induced fluorescence (PLIF).

Although recognized early as a potential method for catalysis research, its use has been very limited and restricted to the ultraviolet/visible spectral regime, meaning several gases important for catalysis, such as CO₂, CO and small hydrocarbons, have remained elusive because of excitation and detection limitations. However, the technical development during recent years in lasers and infrared detection capabilities together with efficient detection and background suppression schemes developed in an earlier study enables the use of PLIF for several of these previously undetectable gases. The first detection of CO₂ to study catalysis was made in a recent study by Zetterberg et al.; however, it was limited to averaged data, lacking the capability of capturing single shot data with sufficient signal-to-noise to really make an impact. However, with further refinements of the experimental set-up and methodology we have been able to use infrared PLIF to capture instantaneous, 2D images of the probed CO₂ gas formed during oxidation of CO over porous supported noble metal catalysts. A schematic of the process is shown in Fig. 1. In this report we highlight the advantage of being able to perform spatially resolved, in situ measurements of the gas phase close to catalysts by means of infrared PLIF. First, we show how the catalytic ignition and extinction of the CO oxidation can be followed for a powder catalyst with a frame rate of 10 Hz, directly visualizing the change in the gas composition close to the catalyst surface. Second, the possibility to measure the CO₂ distribution above two catalysts that are simultaneously situated in the chamber is presented, and how the presence of the two samples affects each other is discussed. Finally, we show that by physically separating the catalytic samples, the differences in activation temperatures can be directly visualized, and activation energies extracted. The study sheds light on several aspects for catalysis research, especially the
possibility to visualize an event, in this case the elusive CO$_2$ product, with high temporal and spatial resolution, at realistic industrial conditions.

Results

Experimental description. In our experiments we used infrared PLIF to image the temperature-dependent dynamics of CO$_2$ close to the surface of catalytic discs during ignition and extinction of catalytic CO oxidation. The samples studied were industrial-like pressed noble metal powder catalysts, and we specifically investigated how the gas distribution around the catalytic discs was changing with sample position, as well as in the presence of two samples in the chamber. In the end we give an example of how to perform combinatorial measurements on three samples simultaneously, without having the samples affecting each other, as a way of screening potential catalysts in the development phase both academically and industrially.

In all our measurements a mass spectrometer, connected to the outlet of the reactor via a leak valve, was used to monitor the global gas composition. The MS signals have a time lag of $\sim 5$ s in the present set-up, compared with the LIF signal (which is almost instantaneous), and the increase in the CO$_2$ signal as the sample ignites is slower. The lag originates from the time it takes for the gas to reach the MS and is dependent on the flow speed, pressure and the volume of the gas has to pass to reach the leak valve.

Measuring CO$_2$ distributions over single-catalyst samples. We first investigated the CO$_2$ distribution over two samples, 2%Pd/CeO$_2$ (hereafter called the Pd-sample) and 2%Pt1%Pd/CeO$_2$ (hereafter called the Pt-Pd-sample). Worth noting is that the percentages given is by weight, meaning that the concentration of active atoms is the same in both samples. To that end we took infrared PLIF snapshots of the CO$_2$ distribution around each catalyst (Fig. 2a,b and Supplementary Movies 1 and 2). The gas flows were 18 ml$_n$ min$^{-1}$ CO, 18 ml$_n$ min$^{-1}$ O$_2$, and 36 ml$_n$ min$^{-1}$ Ar at a total pressure of 105 mbar. The temperatures discussed in the text refer to the thermocouple temperatures.

Already at 137 °C (time I, Fig. 2a,d) the fluorescence signal close to the sample surface increased slightly, indicating the presence of CO$_2$, as both samples started to ignite. At 165 °C the Pd-sample ignited (time II, Fig. 2b), which was manifested as a circularly shaped CO$_2$ distribution above the sample that decreased away from the sample surface. This is expected because the CO$_2$ distribution around the sample is mainly determined by diffusion. In contrast, the fluorescence measured above the Pt-Pd-sample, while stronger than that measured at 137 °C, was still low at this temperature, thus providing evidence for a low catalytic activity (time II, Fig. 2e). Only when the temperature was ramped up to 220 °C the Pt-Pd-sample ignited, resulting in a circularly shaped CO$_2$ distribution similar to the one observed for the Pd-sample at 165 °C (time III, Fig. 2f).

Above these temperatures, both samples reached a steady-state CO$_2$ production, which resulted in only small changes in the distribution of the gas. A slight drag towards the right can be seen, which can be attributed to the gas flow passing from left to right in the image. At 250 °C, the samples reached equilibrium, the gas distribution was steady and the CO$_2$ concentration had stopped to increase.

**Figure 2** | CO$_2$ distribution over two single-catalyst samples. CO$_2$ distribution over two single-catalyst samples at different temperatures at a total pressure of 105 mbar, infrared PLIF single-shot images of the CO$_2$ distribution over (a–c) Pd sample and (d–f) Pt-Pd-sample surface at different temperatures (see also Supplementary Movies 1 and 2). For both samples, we also show (g) the fluorescence signals measured 1 mm over the surface of the samples, calibrated to CO$_2$ partial pressure below the shaded area, (h,j) the calibrated MS profile of CO, O$_2$, and CO$_2$ for the Pt-Pd and Pd samples, respectively, (j) the temperature of the samples’ surface (red and blue) and sample holder (c) and (k) the CO$_2$ gradient (calibrated below the shaded area) from $\sim 0.2$ mm above the sample as a function of temperature. The roman numerals indicate times during the experimental measurement that correspond to the time when the snapshots shown in Fig. 2a–f were recorded.
The fluorescence signal was extracted 1 mm above each sample’s surface from each snapshot image (Fig. 2g). Furthermore, we measured the MS signal—normalized to the known initial partial pressure of CO and O₂; CO₂ was scaled to match the observed conversion of CO—to elucidate the signal’s dependence on temperature (Fig. 2h,i), and the temperature of the samples’ surface and sample holder (Fig. 2j).

One way to investigate the catalytic activity is to study the spatial gradient vertically away from the Pd-sample, something infrared PLIF gives the opportunity to do on a single-shot basis. The gradient was followed in time as a function of temperature (Fig. 2k). From the image it can then be seen that already in the kinetically controlled regime, at 100°C, there is a significantly higher CO₂ concentration close to the surface than further away. Just before ignition the partial pressure of CO₂ ranges from ~1.5 mbar at 0.2 mm above the surface to 0.8 mbar at 2 mm from the surface (the latter being close to the pressure observed by the MS at the outlet of the reactor).

For both samples, the concentration plateaus both in the fluorescence and in the MS signal show that the reactions are limited by the CO diffusion to the catalyst, which occurs almost immediately after ignition, and that all the CO molecules that reach the surface are oxidized.

When the temperature was ramped down the signals concomitantly decreased as the catalytic activity of the samples decreased. The temperature at which the Pd-sample extinguishes is lower (133°C) than the corresponding temperature at which the Pt–Pd extinguishes (199°C), which mimics the corresponding trend in the ignition process where corresponding temperatures are 165 and 218°C, respectively. The difference in temperatures for ignition and extinction is in agreement with previous studies of supported Pd and Pt catalysts.

In general, the averaged infrared PLIF signals (Fig. 2g) were in agreement with the ones obtained by MS (Fig. 2h,i), with only a slight delay of the latter relative to the former because of the time required for the gas distribution around the sample to reach the MS. The instant at which the samples became active also coincided with an increase in the surface temperature of the samples because of the exothermic nature of the reaction (Fig. 2j).

Although the accuracy of the measured absolute temperatures was ~10–20°C, these measurements provided an additional validation and understanding of the dynamics of the gas distribution during the experiment. The temperature measurements also did not suffer from the time-lag associated with the MS measurement, thus making a more accurate measurement of the activation temperatures possible. In the present case, the ignition can in principle be monitored by the thermocouple or better the infrared camera; however, for many other reactions (or for low concentrations of CO), the reaction is not as strongly exothermic as in the case of CO oxidation, disqualifying the thermocouple reading as a probe for the ignition.

Simultaneous measurements of CO₂ above two samples. To demonstrate the versatility and high-resolution measurement capabilities of infrared PLIF, we next measured the CO₂ distribution over the two samples discussed in the previous section, simultaneously and under the same conditions as above (18 ml min⁻¹ CO, 18 ml min⁻¹ O₂ and 36 ml min⁻¹ Ar at a total pressure of 105 mbar). To that end, we placed the two catalytic samples next to each other in the reactor (~8 mm apart) and measured and analysed the infrared PLIF signal, showing that it is possible to distinguish the CO₂ distribution around each sample.

The results of the temperature-dependent infrared PLIF measurements are shown in Fig. 3, alongside measurements of the MS signal, and the temperatures of the samples’ surfaces and holder. We found minimal activity already at T=136°C (Fig. 3a) and the Pd-sample ignited at a temperature of 170°C (Fig. 3b), resulting in the formation of a cloud-like CO₂ distribution similar to the one observed in the single-sample measurements. The
probing the corresponding CO2 distribution. As the temperature was further increased, the Pt–Pd sample also became active at ~221°C (Fig. 3c), and a much larger cloud of CO2 is now visible above the surface of the sample holder. However, the distributions are still highly localized and separable above each of the samples.

At 250°C (Fig. 3d), both samples reached equilibrium and the gas distribution around the samples was found to change very little with further increase in the temperature. The CO2 concentration in the chamber was inhomogeneous, with a somewhat stronger fluorescence signal detectable on the right-hand side of the reactor, which can be attributed to the gas flowing through the reactor from left-to-right.

When the temperature was ramped down, the Pt–Pd sample was first to extinguish (Fig. 3e) soon thereafter followed by extinction of the Pd-sample (Fig. 3f). The ignition/extinction events for both samples give rise to corresponding signatures in the LIF trace, MS signal and temperature data (Fig. 3g–i). This experiment shows the potential of laser diagnostics and the advantage of having 2D, spatially resolved, nonintrusive measurements on one and two samples, the only modification being that the gas was directed to flow through the three tubes. The tubes ended inside the middle of the vacuum chamber where the laser sheet was placed as close as possible (<1 mm) to the exits of the tubes. In this way the gas originating from each individual tube could be probed simultaneously by the laser. In each of the three tubes a monolith sample was placed, each containing Pd/CoO2, Pt/CoO2 and Pt/Al2O3, respectively.

We performed similar measurements, as with the one- and two-sample cases, of the infrared PLIF, MS and temperature of the samples, as a function of temperature (Fig. 4), but at higher pressure, 1 bar.

In contrast to our previous collection of snapshot images of the infrared PLIF, we here show averaged (over 10 laser pulses) infrared PLIF images that are measured at the exit of the three tubes (Fig. 4a–d). At 70°C (Fig. 4a) none of the samples had ignited and no infrared PLIF signal was visible. As the temperature was increased, the Pd/CoO2 sample ignited at 180°C (Fig. 4b), followed by the Pt/CoO2 at 278°C (Fig. 4c) and Pt/Al2O3 at 352°C (Fig. 4d). The signals were not centred in the tubes because of the low flow out from the tubes and because the outlet was placed at the bottom of the reactor.

The onset of ignition for each of the samples yielded an abrupt increase in the averaged infrared PLIF signals at the exit of the tubes (Fig. 4e). This contrasts the MS results where it is not possible to extract the ignition times and temperatures for the different samples (Fig. 4f). While the MS signal changes with temperature, the changes are not as pronounced as in the infrared PLIF data, which makes it impossible to tell from which sample the signal originates. This also opens up for the possibility of extracting quantitative data for the individual catalysts. Activation energies are calculated from the three Arrhenius plots (Fig. 4h) that are extracted from the infrared PLIF signals (Fig. 4g). As expected, the activation energy of 0.25 and 0.53 eV found for the two CoO2-supported samples are lower than for the Pt supported

Probing the CO2 production from three samples in parallel.

Because of the possible interaction of the samples as demonstrated above, we also applied and demonstrated the versatility of the technique by probing the CO2 production originating from three separate samples simultaneously and, in parallel, by placing these into three separated flow tubes. We pursued this solution for situations in which having more than one sample in the reactor changes the reaction of the adjacent samples and vice versa. To address this problem we developed our reactor to have the possibility to include three tubes (see Methods section). The experimental set-up used the same gas system as in the experiments on one and two samples, the only modification being that the gas was directed to flow through the three tubes. The tubes ended inside the middle of the vacuum chamber where the laser sheet was placed as close as possible (<1 mm) to the exits of the tubes. In this way the gas originating from each individual tube could be probed simultaneously by the laser.

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by $\text{Al}_2\text{O}_3$ (1.05 eV). This is also in good agreement with what is reported in literature\textsuperscript{2,3,33}. In contrast, the overlapping $\text{CO}_2$ MS signals complicate the analysis of finding the individual reaction rates for each of the three catalysts and thus constrains the possibility to achieve the activation energy with the MS. The infrared PLIF method could therefore be used to study several catalysts in parallel in a way that has not been possible before.

Discussion

The present report shows that the technical development of lasers, detectors and data treatment during the last 15 years enables direct 2D detection of small molecules relevant for catalysis previously not attainable by LIF. To detect $\text{CO}_2$ at elevated temperatures and realistic gas conditions, it is necessary to excite the molecule with a wavelength of 2.7 $\mu$m, demanding a high-energy laser with a respectable power and narrow linewidth. Further, a fast gateable infrared camera with the ability to detect the fluorescence light at 4.3 $\mu$m is needed, since a fast subtraction scheme is required to remove the otherwise completely dominating thermal background, a short gate time (ns–μs regime) and a high enough frame rate makes this possible. Thus, both laser source and detector used in the present investigations are nonstandard making the combination truly unusual, and have not previously been used for catalysis-related studies.

With PLIF, whether in the infrared or ultraviolet/visible regime, the gas distribution around a catalyst can be visualized with high spatial and temporal resolution (below 500 $\mu$m and down to $\sim$50 $\mu$m depending on excitation wavelength and from 10 μs down to below 10 ns for a single snapshot) with the only disturbance being the excitation of the interrogated species. For the direct product of CO oxidation, this has not been possible until now. The results presented here is an important step for a better understanding of gas phase-related phenomena in catalysis, where dynamics can be studied that are otherwise often hidden in averaged data.

The study implies several new aspects for catalysis research, for example, with PLIF it is possible to measure the gas surrounding the sample at realistic pressures, revealing the actual gas composition close to the surface previously not attainable, for a correct interpretation of the active site or phase. The study also shows with images that by following the gas distribution in time it is possible to distinguish whether the entire catalyst or only part of it is active, or by directly comparing two catalysts decide which has the lowest activation temperature.

By combining the present gas phase measurements with simultaneous X-ray diffraction measurements\textsuperscript{34}, the correct active site/phase should become available. In this way, it should be possible to determine the surface structure and the gas composition close to the surface of the catalyst, previously simultaneously unattainable properties. Furthermore, our study shows how PLIF applied to catalysis has a potential for simultaneous characterization or combinatorial studies of industrial catalysts in a straightforward way. While infrared PLIF applied to catalysis is just barely developed, a present drawback of optical and laser-based methods is the need for specialized reactors with optical access with at least one, but often as many as three transparent windows. Further, the present relatively complicated experimental set-up and data analysis limits the use to experienced and trained researchers.

To this end, we are in the process of developing more standardized reactors, lasers and software suitable for (infrared) PLIF, with the possibility of applying an additional experimental technique. An example of a step in this direction is the development of a reactor towards simultaneous synchrotron radiation and laser measurements, where surface and gas phase information can be extracted simultaneously under the same conditions and at the same sample.

Using modern laser and detection techniques (not limited to the infrared regime), the experiments presented here can be extended to a vast number of gas species, such as $\text{CO}$, $\text{CH}_4$, $\text{NH}_3$ and NO. Our present experiment highlights the principle of the experiment and the spatial resolution provided applying infrared PLIF to catalysis, where flows and gas distributions can be measured instantaneously in 2D, something conventional techniques such as MS, GC and FTIR lacks, and provides a tool that in principle can be used simultaneously with synchrotron-based measurements.

Methods

Infrared PLIF. The principles of infrared PLIF are (Fig. 1) as follows: (1) a laser excites a vibrational/rotational level in the molecule of interest; (2) the molecule fluoresces in response to the laser excitation by emitting light at a wavelength that is known a priori; (3) the emitted fluorescence is detected and analysed. In our study, the infrared laser beam was generated by difference-frequency mixing the output from a dye laser (Sirah PRSC-D-18) at 763 nm with the fundamental frequency from a Nd:YAG laser (Spectra Physics, ProVue 290-10) at 1.064 nm in a LiNbO$_3$ crystal, yielding a 2.7-μm laser pulse (with a pulse energy of 4 mJ, 5 ns pulse duration and the linewidth estimated to 0.025 cm$^{-1}$)\textsuperscript{35}. The output from the laser was used to probe the P(12) line of the (60P$^0$)$\rightarrow$(10P$^0$) combination band of the $\text{CO}_2$ molecules in the vicinity of the catalyst, and the fluorescence at 4.3 $\mu$m was detected by a 2D infrared camera (Santa Barbara Focal Plane, SBF LP134). The infrared PLIF images visualize the $\text{CO}_2$ distribution (Fig. 1c) in a 25 × 13-mm$^2$-sized rectangle above the catalyst. The images were collected every 0.1 s and with a temporal resolution for each frame, limited by the exposure time of the camera, of 15 μs, and the spatial resolution was ~400 μm and limited by the thickness of the lasersheet. The detection limit for $\text{CO}_2$ was estimated to 100 p.p.m. (or 0.1 mbar) in the present measurements. A schematic describing the laser set-up, optics and the collection of the images is shown in the Supplementary Fig. 1. The infrared background was subtracted with a scheme presented in ref. 29.

The $\text{CO}_2$ fluorescence intensity has been calibrated to mbar for concentrations lower than ~2 mbar. This is made possible by making calibration measurements at known $\text{CO}_2$ concentrations and temperatures, creating a calibration curve. As the temperature field in the reactor is inhomogeneous, it has to be corrected for in order to give a correct representation of the $\text{CO}_2$ concentration. Infrared PLIF images with a homogeneous $\text{CO}_2$ distribution is therefore collected at temperatures matching those of the experimental data. While the fluorescence signal is temperature-dependent, these images represent the temperature field and can be used to compensate the measurement data. In this way not only the density differences due to temperature is taken into account but also the difference in polarization. The dependence of fluorescence signal on temperature is covered more thoroughly in the Supplementary Methods section and is demonstrated in Supplementary Fig. 2.

Reaction chamber. The experiments were carried out in a cubical stainless steel reactor cell with a total volume of 240 ml. The samples were placed on a Mo sample holder in the middle of the reactor. The samples could be viewed from four different directions through four CaF$_2$ windows. The Mo sample plate was heated by a boralic electric (Métaux Géomatiques Systèmes Engineering, BN) held by two Ta rods that were attached to current feed-throughs and connected to a 20-A power supply. The samples were thus indirectly heated via the Mo plate and the temperature of the sample holder was measured with type-C thermocouple. The power supply was controlled via a LabView programme in order to increase and decrease the temperature in a controlled way. A schematic of the experimental set-up is shown in the Supplementary Fig. 1.

The surface temperature of the samples was measured using an infrared camera (FLIR P620); however, as the emissivity changes with temperature, it is hard to get an absolute temperature from this measurement. It is, however, a very good indicator of when the sample ignites.

The gas flows were 18 ml min$^{-1}$ $\text{CO}$, 18 ml min$^{-1}$ $\text{O}_2$ and 36 ml min$^{-1}$ Ar at a pressure of 105 mbar for the first two experiments with one and two samples in the reactor.

A premixed 10% $\text{CO}$ in Ar was used for calibration purposes. The gases were introduced into the reactor cell via individual Bronkhorst mass-flow controllers (Bronkhorst EL-FLOW, 50 mln min$^{-1}$) that can vary the gas flow from 1 to 50 mln min$^{-1}$. To keep the pressure constant, a pressure controller (Bronkhorst EL-PRESS) was attached to the gas outlet. The gas composition was studied by a quadruple mass spectrometer (Pfeiffer PrismaPlus QMG220), connected to the reactor outlet via a leak valve.
The samples. The supported noble-metal catalysts were prepared by incipient wetness impregnation targeting the same molar amount of noble metal atoms. The alumina (Puralon Ss 200, Sasol) and ceria (99.5 H. S.A, 514, Rhône-Poulenc) support materials were first thermally stabilized by a treatment at air in 600 °C for 2 h. Each support was then dispersed in an aqueous solution consisting of distilled water and the relevant concentration of noble metal precursor, tetraammineplatinum(II)nitrate (4.0 wt.% (NH₄)₂Pt(NH₃)₄), Alfa Aesar GmbH & Co. KG) and/or tetrachloropalladium(II)nitrate (4.6 wt.% (NH₄)₂PdCl₄), Alfa Aesar GmbH & Co. KG) to obtain the desired noble metal loading, that is, 4%Pt/alumina, 4%Pt/ceria, 2.2%Pd/ceria and 1.1%Pd–2%Pt/ceria (% refers here weight percentage). For the co-impregnation of platinum and palladium, the noble metal precursors were completely mixed together to increase the interaction between the noble metal complex and the support, the pH of the solution was adjusted by NH₄OH addition taking into account the isoelectric point of each oxide. The obtained slurry was then stirred for 20 min, frozen with liquid nitrogen and freeze-dried for 12 h to preserve high noble metal dispersion. The resulting powder was dried for 12 h to preserve high noble metal dispersion. The resulting powder was divided into the smaller tubes where monolith samples (20 mm long and 3-mm thick) were fitted with a CF16 end to connect to the cubical reaction cell described above, and the smaller tubes are placed in such a way that they end in the middle of the cubical reaction cell. The reactor was heated by a resistance heating-wire coiled around the outer fused silica (FS) tube. The tube reactor consists of an outer fused silica (FS) tube with three smaller FS tubes inside. The larger tube has a diameter of 16 mm and is fitted with a CF16 end to connect to the cubical reaction cell described above, and the smaller tubes are placed in such a way that they end in the middle of the cubical reaction cell. The reactor was heated by a resistance heating-wire coiled around the tube and the temperature was measured with a type-K thermocouple placed in the centre of the larger tube between the smaller tubes. The CF16 end of the larger tube was used to connect to the CF40 cube and the smaller tubes were placed such that they ended in the middle of the cube. The gas was supplied through the large tube, in which the gas was divided up into the smaller tubes where monolith samples (20 mm long and 3-mm thick) were placed. The space between the large and the small tubes were sealed with quartz fibres, to prevent the gas from flowing through the small tubes. The small tubes ended centred in the reaction cell and the laser sheet was placed as close as possible to the tube ends, in order to probe the exiting gas. The gases were regulated and pressure-controlled in the same way as in the measurements with one and two samples. The flow fed through the tubes consisted of 5 ml·min⁻¹ CO, 5 ml·min⁻¹ O₂ and 40 ml·min⁻¹ Ar at a pressure of 1.000 mbar.

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Author contributions
J.Z.E. performed the measurements and did the data evaluation together with S.B. and had the major responsibility for preparing the paper (including SI), J.E. designed the reactor for combinatorial studies and took part in and evaluated those measurements. J.G. designed the reactor and took part in the development of the analysis methods, E.L. and P.A.C. wrote part of the paper, J.Z.H. made calibration measurements for quantitative CO₂ profiles, E.C.A. prepared the samples, and M.A. and E.L. supervised the project.

Additional Information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

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