Product gas evolution above planar microstructured model catalysts—A combined scanning mass spectrometry, Monte Carlo, and Computational Fluid Dynamics study

M. Roos,¹ J. Bansmann,¹ D. Zhang,² O. Deutschmann,² and R. J. Behm^{1,a)} ¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany ²Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), D-76128 Karlsruhe, Germany

(Received 19 May 2010; accepted 14 July 2010; published online 2 September 2010)

The transport and distribution of reaction products above catalytically active Pt microstructures was studied by spatially resolved scanning mass spectrometry (SMS) in combination with Monte Carlo simulation and fluid dynamics calculations, using the oxidation of CO as test reaction. The spatial gas distribution above the Pt fields was measured via a thin quartz capillary connected to a mass spectrometer. Measurements were performed in two different pressure regimes, being characteristic for ballistic mass transfer and diffusion involving multiple collisions for the motion of CO₂ product molecules between the sample and the capillary tip, and using differently sized and shaped Pt microstructures. The tip height dependent lateral resolution of the SMS measurements as well as contributions from shadowing effects, due to the mass transport limitations between capillary tip and sample surface at close separations, were evaluated and analyzed. The data allow to define measurement and reaction conditions where effects induced by the capillary tip can be neglected ("minimal invasive measurements") and provide a basis for the evaluation of catalyst activities on microstructured model systems, e.g., for catalyst screening or studies of transport effects. (D 2010 American Institute of Physics. [doi:10.1063/1.3475518]

I. INTRODUCTION

Spatially resolving mass spectrometry has become an important tool in heterogeneous catalysis research, especially for high-throughput measurements and screening experiments.^{1,2} In order to evaluate the activity of a large number of catalysts in parallel, these are loaded into a bundle of parallel microreactors and the composition of the gas streams exiting from the respective microreactor is analyzed by a scanning capillary probe, which is connected to a mass spectrometer and successively positioned above the different outlets of these microreactors.^{3–7} Alternatively, the different catalysts are arranged in two-dimensional arrays on a planar, catalytically inactive substrate. In that case, the catalytically active materials are either located in individual wells⁸ or they are deposited, in an "open" design, in adjacent fields on the substrate.⁹⁻¹³ Often, the reactant gases are provided via a second capillary attached to the sensing capillary, which is either concentric or parallel to the detector capillary. Finally, a different application of spatially resolved mass spectrometry should be mentioned, which aims at studying the progress of the reaction along the catalyst bed by analyzing the gas composition at different positions along the reactor.¹⁴⁻²⁰ In that case, the orifice of the capillary is placed at different positions along the catalyst bed. This way, the influence of existing gradients (e.g., variation of partial pressure of gases and/or temperature) within the catalyst bed can be evaluated.

In addition to catalyst screening, scanning mass spectrometry measurements on planar model catalysts can also be used for studying the role of local inhomogeneities in the catalytic activity and of transport effects in catalytic reactions. By evaluating the product distribution above neighboring active fields on a microstructured model catalyst and its dependence on parameters such as the reactant partial pressures, the substrate temperature, or the size and separation of the active fields, effective interactions between different catalytically active regions on a sample surface can be studied and possible mesoscopic transport effects in these reactions can be mapped out. In all of these studies, it is of utmost importance that the probe, in this case the probing capillary, does not or at least only in a well-defined way affect the measured reactant and product distributions, i.e., it should be minimally invasive analogous to the measurements in fixed-bed reactors.¹⁴

These questions are topic of the present paper, where we report on spatially resolved mass spectrometry measurements of the reactant and product distribution above differently shaped active Pt microstructures on an inert SiO₂ substrate, and their changes upon varying the vertical distance between substrate surface and probe, the reaction pressure, and the shape of the active microstructure. The oxidation of CO is used as test reaction. For a detailed understanding of the measured data, the number of CO₂ product molecules, which are reaching the orifice of the sensing capillary at a given position of the capillary relative to the active microstructure and are thus detected by the mass spectrometer, is simulated by Monte Carlo techniques by computing the tra-

133, 094504-1

^{a)}Author to whom correspondence should be addressed. Electronic mail: juergen.behm@uni-ulm.de.

jectories of the CO₂ molecules and their collisions with other gas phase molecules. Furthermore, shadowing effects introduced by the presence of the capillary sensor and its specific geometry (here, a circular orifice with \emptyset =70 μ m), which may reduce the reactant partial pressures in the space between capillary and substrate and hence the local reaction rate in that area, are evaluated by fluid dynamics calculations, which consider the specific geometric configuration of the tip orifice and the catalytically active fields, as well as the physical properties of the involved gas species CO and O₂. CO₂ is neglected in these calculations because of the very low partial pressures.

The final objective of this study is to (i) quantitatively evaluate coupled reaction and transport processes in a running catalytic reaction while taking minimum influence on the reaction conditions and to (ii) understand the gas transport between sample and the tip of a detecting capillary to quantitatively analyze the measured product gas evolution. The microstructured model catalysts were prepared by lithographic techniques similar to those used previously for preparing microstructured Au/TiO₂ model catalysts.²¹ The scanning mass spectrometer setup is largely identical to one described recently.²² In contrast with other open designs, the probing capillary in our setup has only a sensing function and is not part of the reactor as, e.g., in the system presented by Johansson *et al.*,^{11,23} where the reactant gases are provided via a thin tube surrounding the probing capillary.

In the following, we will, after a brief description of the experimental setup and the experimental and theoretical procedures, first present the results of the spatially resolved mass spectrometric measurements, considering two different shapes and sizes of active Pt microstructures and two different pressures of the reaction atmosphere (Sec. III A). Subsequently, shadowing effects caused by the presence of the capillary tip are simulated in fluid dynamics calculations (Sec. III B), the distribution of CO₂ product molecules is modeled in Monte Carlo simulations (Sec. III C), and finally the lateral resolution of these measurements is assessed quantitatively by evaluating the origin of the detected CO_2 molecules on the sample relative to the capillary orifice (Sec. III D). The main results of the study are summarized in Sec. IV.

II. METHODOLOGY

A. Experimental

The scanning mass spectrometer setup used for measuring the spatial evolution of reactant gases was described in detail elsewhere.²² Since then, the setup was modified by (i) exchanging the positions of the quadrupole mass spectrometer (QMS) and of the turbomolecular pump for differential pumping, such that after leaving the capillary the gas molecules pass directly through the ionization room of the QMS, which is oriented normal to the molecule flight direction, and then hit the rotor of the turbomolecular pump. The latter is oriented along the axis of the flight path of the molecules. Second (ii), a larger turbomolecular pump (Varian TV 301 Navigator, 250 1 s⁻¹) was used for pumping the analysis chamber. These changes result in a more efficient pump-off



FIG. 1. Schematic drawing of the capillary tip used for product gas sampling showing (a) the capillary geometry and (b) the principle of simulation. The yellow circle represents the capillary orifice, which is surrounded by the cylindrically shaped capillary wall (light gray area). The catalytically active surface area is subdivided into finite elements representing point sources for desorbing CO_2 molecules. Desorbed molecules, which move between sample surface and capillary tip, interact with molecules in the gas phase (mainly O_2), as described by the MC simulations. This region between substrate and capillary plane is divided into finite radial elements, with characteristic properties of the local gas phase as determined by the CFD calculations (pressure, temperature, and velocity components). Molecular trajectories are followed until the capillary plane is reached. For comparison, an optical microscopy picture of the end of a capillary with comparable dimensions to that used for the present experiments is shown in the inset.

of the gas molecules after passing the ion source of the QMS, which lowers the overall background of the analysis chamber and thus increases the sensitivity of the QMS. Additional, minor modifications were made by adding 2 micrometer screws to the sample stage, which allows a precise orientation of the sample surface. To guarantee an accurate adjustment of the pressure in the reaction chamber (especially in the millibar regime), a bellow valve (Parker, P-Series) was added to the system, which bypasses the existing UHV gate valve. To reach higher reaction pressures, the main gate valve can be closed during the measurement and the pressure is solely adjusted via the bellow valve by controlling the outflow of the reactant gases. Furthermore, in order to obtain a well-defined tip geometry, the constricted end of the capillary was drawn to a uniform cylindrical channel of about 3 mm in length with inner and outer diameters (capillary orifice and capillary wall) of 70 and 300 μ m, respectively [Fig. 1(a)].

The Pt structures (thickness of 200 nm) were produced by vapor deposition on a Si(111) substrate, using standard optical photolithography under clean room conditions. Using this procedure, Pt structures were prepared where a single Pt field with a well-defined shape is located in the center of each sample (surface area of $10 \times 10 \text{ mm}^2$). For cleaning, all the samples were annealed at 425 °C in O₂ (30 min, 3.6 mbar) prior to the reaction measurements. All measurements were performed in an O₂ excess to avoid CO_{ad} blocking of the active surface, at a CO:O₂ ratio of 1:14. Using a constant heating power of 15 W resulted in sample temperatures of 305 and 325 °C at 0.37 and 3.7 mbar, respectively.

Sample and sample holder were mounted on a table whose position could be varied in a controlled way along all three coordinates (maximum scan range: 20 mm along the xand y-axes and 15 mm along the z-axis). The scans were performed by stepping the sample along the x-directions and return (step width 25 μ m). After each step, the O₂, CO, and CO₂ partial pressures were measured (waiting time after each step is 2 s to reach steady-state conditions). The separation between sample surface and capillary tip was controlled by a fiber optic displacement sensor and kept constant to within $\pm 1 \ \mu m$ during the measurements. By measuring the local gas composition above the sample surface as function of lateral and vertical displacement relative to the center of the Pt field, a three-dimensional diagram is obtained, reflecting the spatial CO₂ product gas evolution originating from the respective underlying field and the related reactant consumption.

B. Computational fluid dynamics

Computational fluid dynamics (CFD) calculations using the commercial software package FLUENT (version 6.2.16) were conducted to obtain details on the flow and pressure patterns between the tip of the capillary and the sample surface toward the capillary orifice [Fig. 1(b)]. Due to the large excess in oxygen, a single-component flow simulation is sufficient to compute the pressure loss between the substrate and the capillary; the resulting pressure variation is then used as parameter in the Monte Carlo (MC) simulations. Because of the similar diffusion properties of CO and oxygen, the computed total pressure also reflects the variation of the CO partial pressure in this regime. The simulations compute the velocity, pressure, and temperature profiles in the gap between capillary and sample. In the simulations, Dirichlet boundary conditions were used for the pressure and temperature at the inlet and outlet, which were taken from the experimental conditions. At the heated substrate surface, noslip and constant temperature boundary conditions were used, while the capillary wall was treated as adiabatic wall, employing Neumann boundary conditions with zero heat flux.

Due to the axial symmetry of the capillary tip, the three independent spatial variables of the steady-state Navier– Stokes equations can be reduced to two: the axial coordinate z and the radial coordinate r with the corresponding components of the velocity vector (u, v) aligned with the cylindrical coordinates (z, r). Hence, two-dimensional simulations of the flow fields and the heat balance were performed in cylindrical coordinates for a set of external geometrical, temperature, and pressure conditions.

C. MC simulations

For the MC simulations, the Pt fields are divided into finite-sized surface elements (square areas with 20 $\times 20 \ \mu m^2$), where the center of each element is considered as local (point) source of product gas molecules (CO_2) . After desorption from the surface, the trajectories of the CO₂ molecules are determined by ballistic mass transport and intermolecular collisions with the gas phase in the region between sample surface and capillary tip. The region included in these simulations is delimited by the sample surface and by a plane parallel to the surface (denoted as capillary plane), which touches the final end of the capillary tip [Fig. 1(b)]. In our model, molecules which finally pass the capillary plane during their motion are evaluated with respect to the lateral position. If they hit the plane outside the capillary wall, they are discarded; if they hit the capillary wall around the orifice, they are elastically reflected analogously to molecules hitting the sample surface, and only the CO₂ molecules impinging on the capillary plane within the orifice area are considered for the detector signal.

The angular distribution of the desorbing CO₂ molecules is described by a cosine distribution^{24,25} and a temperature of 1700 K is assumed to describe the velocity of the desorbing CO₂ molecules.^{26,27} Desorption of CO₂ molecules from the different centers (surface elements) is treated sequentially. Each time, the polar and the azimuth angle determining the direction of the desorbing CO2 molecule are chosen by the MC simulation according to the distribution function of the cosine distribution (polar angle) and an isotropic distribution (azimuth angle), respectively; the mean velocity of the molecule at 1700 K was taken as starting velocity. (Tests using a velocity distribution which is, per se, more realistic, showed no significant differences in the overall characteristics). Subsequently, the probability for passing the first volume element is calculated by selecting the free path length from the Poisson distribution of path lengths in that element, where the latter depends on the pressure and the gas temperature in that element and on the velocity of the CO_2 molecule. If the free path length exceeds the size of the volume element, the CO₂ molecule will pass this element and enter the next element, where the same process starts again with updated local gas properties. If the selected free path length is lower than the element size, it comes to a collision with another molecule, most likely with an O₂ molecule under present reaction conditions, due to the considerable O_2 excess. These events are described as elastic collisions of two point masses representing the CO₂ molecule and an O₂ molecule of the gas phase; the Maxwell-Boltzmann velocity distribution function is used to select the velocity components (V_x, V_y, V_z) of the O₂ molecules. Collisions with CO molecules are not separately evaluated due to their low concentration in the gas mixture and the small mass difference between CO and O₂. In order to get reliable statistics, the

simulation was repeated 1000 times per surface element (see below) and capillary position.

The additional information about the macroscopic behavior of the gas phase around the capillary orifice obtained in the CFD calculations (gas flow, pressure variation, and heat dissipation) can be embedded in the MC simulations. For this purpose, the region between the sample surface and the capillary orifice is divided into finite radial volume elements, each of which is characterized by averaged values of the local pressure, temperature, and radial and axial velocity components, as derived from the CFD calculations [see Fig. 1(b)]. The size of the elements (radial/axial extension of elements) varies between 1 and 10 μ m, depending on the capillary height. The molecular flow and the heating of the gas phase close to the sample surface enter into the MC simulations, when recalculating the velocity components of the CO₂ molecules after collisions in the respective elements within the gas phase, by adding the velocity components from the flow field to the velocity of the O_2 molecules and by considering the local gas temperature in the Maxwell-Boltzmann velocity distribution function of the O2 molecules, respectively. Along the line scans, the MC simulations were performed every 25 μ m.

III. RESULTS AND DISCUSSION

A. Scanning mass spectrometry measurement of the spatial gas evolution and distribution

The spatial evolution of CO₂ product molecules and the position dependent reactant partial pressures above the two different Pt microstructures were evaluated at two different pressures. The first Pt microstructure has a quadratic shape ($800 \times 800 \ \mu m^2$), while the second one has a rectangular shape ($200 \times 10\ 000\ \mu m^2$). The gas pressures used in these experiments (0.37 and 3.7 mbar) result in different mean free path lengths of about 270 and 27 $\ \mu m$, respectively, for CO₂ molecules in an O₂ environment at 600 K.

Figure 2 shows the results of spatially resolved SMS measurements on the evolution of CO₂ and consumption of CO above a Pt stripe at 3.7 mbar. (The O_2 partial pressure was measured as well, but is less informative because of the rather small variations.) The data were acquired in line scans across the Pt structure parallel to the surface [upper panel of Fig. 2(a) at different vertical distances between capillary orifice and sample surface, with the distances ranging from values close to zero up to 1000 μ m. At close distances between sample and orifice, the SMS signals show pronounced peaks (CO₂) and depressions (CO) above the catalytically active field, which broaden and loose in intensity with increasing vertical distance. The ion currents measured by the scanning mass spectrometer above the center of the Pt structure are additionally plotted in the lower panel of Fig. 2(a) in order to demonstrate the decrease (increase) of the CO_2 (CO) ion current with increasing separation between sample surface and capillary tip. With increasing height of the capillary tip relative to the sample surface, the CO partial pressure increases until it reaches the preset value in the reaction chamber. At the same time, the CO₂ signal decreases. It should be noted that the CO₂ signal starts to decrease also



FIG. 2. Spatial distribution of reactant (CO) and product (CO₂) partial pressures above a 200 μ m wide Pt stripe (length: 10 000 μ m) at 3.7 mbar and 600 K determined by scanning mass spectrometry, showing the (local) consumption and production of reactant and product gases. (a) Line scans across the Pt structure at different capillary heights (upper panel); (b) two-dimensional plots representing a cross-sectional view of the spatial variation of the partial pressures of the components. The lower panel of (a) shows the variation of the SMS signal above the center of the Pt structure with increasing capillary height.

when the capillary tip is very close to the sample surface. This effect is related to a shadowing introduced by the capillary tip. The fact that the reactant gases have to pass the narrow channel between capillary wall and sample surface limits the CO conversion in this distance regime (for details, see Sec. III B).

Two-dimensional plots representing a cross-sectional view of the lateral variation of the gas pressures above the Pt stripe are shown in Fig. 2(b). The upper panel illustrates the distribution of the CO₂ product gas originating from the underlying Pt structure (indicated by the black bar in the center of the x-axis) and the lower panel represents the correlated spatial variation of CO in the gas phase caused by consumption in the catalytic reaction and gas flow through the capillary. The gas distributions in the two graphs are not exactly complementary because the increase of CO₂ pressure (CO₂ formation via desorption from the Pt field minus CO₂ losses



FIG. 3. CO₂ product partial pressure above a square Pt field (800 \times 800 μ m², left panels) and a Pt stripe (200 \times 10 000 μ m², right panels) at 0.37 (upper panels) and 3.7 mbar (lower panels). The line scans displayed in the center were taken at different vertical distances between capillary orifice and sample surface for capillary heights of (a) 4, 16, 26, 36, 73, 110, 355, 875, and 964 μ m; (b) 3, 13, 24, 34, 79, 131, 291, 701, and 951 μ m; (c) 4, 14, 35, 65, 108, 213, 353, 623, 873, and 973 μ m; and (d) 4, 15, 37, 76, 126, 193, 298, 438, 708, and 958 μ m. The signal intensities of the line scans decrease in this order, except for the gray colored data points (*p* = 3.7 mbar) related to the lowest capillary height (4 μ m). The gray areas in the graphs represent the lateral extents of the Pt fields and the contour plots related to the respective sets of line scans visualize the two-dimensional product gas evolution above the fields.

through the capillary) and the loss of CO (CO consumption on the Pt field plus CO losses through the capillary) are related to different mechanisms. The decrease of the CO signal close to the surface also far aside the Pt field (and thus far away from the CO sink) again indicates a pressure drop induced by the presence of the capillary tip (shadowing by the capillary tip).

The influence of the geometry of the Pt microstructure and of the total pressure in the reaction chamber on the CO₂ evolution above the Pt structures is illustrated in Fig. 3, which shows SMS measurements over a quadratic Pt field (left panels) and over the Pt stripe described above (right panels) at two different pressures: 0.37 (top) and 3.7 mbar (bottom). All graphs in this figure have identical x-axes (from -950 to $+950 \ \mu$ m); the lateral displacement denotes the lateral position of the capillary orifice relative to the underlying fields. To facilitate a direct comparison of the data presented in this figure, the scales of the y-axes of the respective horizontal graphs as well as the pressure levels of the colors in the contour plots are identical over the two different structures.

The characteristic features of the line scans (CO₂ signal) in the central part of Fig. 3 are obviously strongly affected by the geometry of the respective underlying Pt fields (marked areas), with the highest CO₂ ion currents measured directly

J. Chem. Phys. 133, 094504 (2010)

above the Pt fields. In contrast to the Pt stripe, the CO₂ intensity shows a pronounced plateau above the broader square field for small capillary heights [Figs. 3(a) and 3(c)], which successively decreases in intensity and width when the capillary is retracted from the sample. When comparing the heights of the CO_2 signals above the center of the square Pt field and the Pt stripe at lower pressure (0.37 mbar), the values are comparable for small capillary-sample distances, although the formation of a plateau above the Pt stripe is not observed due to the smaller lateral size. In both cases, the CO₂ signal decays rapidly to a constant signal corresponding to the CO₂ background in the analysis chamber, when the orifice is no longer located above the Pt area. It has been shown earlier that the characteristics of this slope are mainly dominated by the distinct geometry of the capillary tip when it is very close to the sample surface.²² At higher pressures (3.7 mbar), the line scans generally exhibit a much rounder and broader shape, which leads to a less pronounced plateau and slower decay of the signal aside the Pt fields. As a consequence, the CO_2 signal does not even reach the CO_2 background level within the range of the measured lateral scan. This behavior is also reflected in the four contour plots. At 0.37 mbar, the presence of CO₂ molecules is mainly limited to the region directly above the Pt fields, indicating a preferred desorption angle perpendicular to the sample surface as expected in the case of a cosine distribution of the desorbing CO_2 molecules. In contrast, at 3.7 mbar, the spatial evolution is more of spherical character, showing that the primary angular distribution of the desorbed CO₂ molecules is disturbed by multiple collisions with other molecules in the gas phase.

Qualitatively, this result agrees perfectly with expectations based on the mean free path of the (product) molecules. Due to the short mean free path of about 27 μ m in the high pressure regime (at 3.7 mbar), the molecules exhibit a much higher number of collisions compared to the pressure regime at 0.37 mbar, while at lower pressures the large mean free path of about 270 μ m enables an almost pure ballistic motion of the CO₂ molecules between the sample surface and the capillary orifice. Thus, for small capillary heights, the slopes of the respective line scans are dominated by the geometric overlap of the capillary orifice and the Pt field in both pressure regimes. With increasing distance, the slopes successively broaden due to the increasing influence of the angular distribution of the desorbing molecules. In the high pressure regime, the much slower lateral decay of the signal amplitude implies a basically different transport mechanism. This is described in more detail together with the simulations in Sec. III C.

B. Computational fluid dynamics calculations

Proper understanding of the shadowing effects caused by the capillary, which were observed in the measurement described in Sec. III A, requires a more detailed analysis of the gas atmosphere and the local pressure in the region between sample surface and capillary. Figures 4(a)-4(d) show the calculated distribution of pressure, temperature, and the velocity components (axial and radial velocity) in the small volume



FIG. 4. Distribution of the (a) pressure p, (b) radial velocity V_{radial} , (c) axial velocity V_{axial} , and (d) temperature T in the gap between sample surface and capillary tip (10 μ m) at 3.7 mbar, computed by 2D CFD simulations. The diagram in the lower panel (e) displays the total pressure underneath the capillary tip at different relative capillary heights vs the lateral position relative to the center of the capillary orifice (marked area: capillary wall). The inset shows the evolution of the pressure at the capillary orifice with decreasing capillary height.

delimited by the capillary tip and the sample surface, which are determined via fluid dynamics calculations, using a capillary height of 10 μ m and a pressure of 3.7 mbar as an example. The pressure decreases toward the center of the capillary, until it reaches a constant value of 2.4 mbar in the region around the orifice [Fig. 4(a)]. Figures 4(b) and 4(c)show that this gradient induces a molecular flow of gases toward the capillary orifice, which is reflected by the radial and axial velocity components. However, the maximum velocity of 1.32 m s⁻¹ is rather small. Furthermore, as seen in Fig. 4(d), the temperature of the gas increases in the region close to the sample due to interaction of the gas molecules with the hot sample surface. The CFD calculations were performed for pressures of 0.37 and 3.7 mbar and for various capillary heights between 2 and 1000 μ m in order to cover the entire range of the SMS measurements presented in Sec. III A.

Figure 4(e) shows the drop of the total pressure for different distances between capillary tip and sample surface $(2-40 \ \mu m)$ at various lateral positions underneath the capillary relative to the center of the capillary (x=0). For capillary heights below 20 μ m, the pressure decreases strongly to an almost constant level in the central region under the orifice. The gradual pressure drop leads to a situation, where the mean free path of the molecules decreases upon moving away from the orifice. This results in an enhanced density of CO₂ molecules around the orifice, and hence increases the probability of CO₂ molecules of being detected. A similar effect is also obtained by the effective transfer of momentum toward the center of the capillary due to the velocity component in that direction in the molecular flow field. Finally, the pressure drop underneath the capillary tip leads also to changes of the local reaction rate. In a simple power law model the change in reaction rate and hence in the number of CO₂ molecules produced per unit area and time can be described by

 $\frac{dp_{\rm CO_2}}{dt} = k \cdot p_{\rm O_2}^a \cdot p_{\rm CO}^b \Rightarrow \frac{dp_{\rm CO_2}}{dt} = k' \cdot p_{\rm total}^n$ with

$$n = (a+b). \tag{1}$$

Here, the partial pressures p_{CO_2} , p_{O_2} , and p_{CO} determine the amount of produced CO₂ molecules and the number of O₂ and CO molecules per volume with the respective reaction orders *a* and *b*. As long as the composition of the gas mixture is constant (and assuming comparable diffusion properties of the two components), the total reaction order *n* can be used to describe the influence of the total pressure. In a previous publication,²² we have shown that reaction orders of *a*=1 (O₂) and *b*=-0.9 (CO) for the CO oxidation on a Pt surface, as they were determined in earlier studies,^{28,29} provide a proper description of the reaction kinetics. Hence, a total reaction order of *n*=0.1 is used to account for variations of the reaction rate in the following MC calculations.

C. Monte Carlo simulations

In order to estimate the capability of quantitative product gas analysis using the scanning mass spectrometer setup described here, the measured CO_2 evolution above the Pt microstructures shown in Fig. 3 is modeled by MC simulations. Following the experiments described in Sec. III A, we will distinguish between the two pressure regimes, with a low pressure regime (0.37 mbar) and a high pressure regime (3.7 mbar). The variations of the local reaction rates were calculated via Eq. (1), using the reactant pressures above the respective position (surface element) determined in the CFD calculations.

1. Monte Carlo Simulations in the low pressure regime

Figures 5(a) and 5(b) show simulated line scans (open symbols) above the square field (a) and the stripe-shaped field (b) at a pressure of 0.37 mbar and, for comparison, the measured CO₂ ion currents (solid symbols) for different capillary heights between 2 and 1000 μ m, according to the heights used for the CFD calculations. The simulated curves were adjusted to the experimental results by a scaling factor,



FIG. 5. Simulated line scans above a (a) square Pt field $(800 \times 800 \ \mu m^2)$ and a (b) Pt stripe $(200 \times 10\ 000\ \mu m^2)$ at 0.37 mbar, obtained by Monte Carlo simulations and considering the variation in reactant pressures derived from CFD calculations (open symbols, capillary heights of 2, 5, 20, 40, 80, 150, 350, 700, and 1000 μ m). For comparison, results from SMS measurements performed at capillary heights of 4, 26, 36, 73, 215, 355, and 964 μ m in (a) and 3, 24, 34, 79, 131, 701, and 951 μ m in (b) are included (solid symbols). (c) shows the evolution of the CO₂ signal above the center of the Pt stripe (lateral displacement x=0). [Note that additional experimental data points have been used where for more clarity the line scans are not included in (b).] The red colored data points denote the corresponding results from the SMS measurements (Fig. 4); green dotted lines: simulation neglecting the variation in partial pressure determined in the CFD calculations [see inset of (c)].

which is constant for all data sets, and a constant offset which corrects for the CO_2 background signal far beside the Pt fields. In general, the simulations are in good agreement with the measured line scans, both in the shape as well as in the height of the signals. Figure 5(c) shows the characteristic decay of the simulated CO_2 ion current (open circles) above the center of the Pt microstructures (here for the Pt stripe as an example) with increasing capillary height; again the measured values are shown for comparison (solid squares).

In order to assess the influence of the shadowing effects, i.e., the pressure reduction under the capillary tip, we performed the MC simulations once using the local pressures determined by the CFD calculations and once without that correction. The resulting differences are illustrated in the inset, which gives an enlarged view of the behavior at small capillary-substrate distances. It shows that simulations including (open circles) or neglecting (green dotted line) the corrections resulting from the CFD calculations differ only for very small distances [below 20 μ m, see inset of Fig. 5(c)]. Even though the total reaction order of the CO oxidation reaction is close to zero (n=0.1) under the present conditions, the local decrease of the reaction rate leads to a noticeable decrease in the CO₂ signal intensity. This effect seems to overcompensate the influence of the molecular flow field, which points toward the capillary orifice and thus is expected to increase the signal intensity by "pushing" the CO₂ molecules toward the capillary orifice. However, the impact of the molecular flow limitations determined by CFD calculations on the MC simulation results can become very significant and has to be included in the simulation at very small substrate-capillary distances.

2. Monte Carlo Simulations in the higher pressure regime

In the following, we will focus on the spatial evolution of the product gas at significantly higher pressures (3.7 mbar) in the reaction chamber where, due to the much shorter mean free path of the molecules, a ballistic mass transport between sample surface and capillary orifice cannot be assumed any more. Local "measured" CO2 partial pressures along line scans above the square Pt microstructure $(800 \times 800 \ \mu m^2)$, either determined by simulations or experimentally, are shown for different relative capillary heights in Fig. 6. When comparing the experimentally obtained line scans to the respective simulated data [Fig. 6(a)], the simulations neither reproduce the generally much more rounded and broader shapes of the measured lines very well, nor do they reveal the characteristic decrease in the signal intensity for very small capillary heights (<20 μ m). Two processes that could possibly explain this discrepancy are (i) a backscattering of CO2 molecules, which have passed the capillary plane outside the capillary, back into the region between substrate and capillary, and (ii) (nonballistic) diffusion of CO₂ molecules from the outside, in particular from areas above the active Pt structure, into this region. This was not considered in the ballistic MC simulations for the low pressure regime, since the mean free path length of 270 μ m is in the order of magnitude of the capillary-sample distance $(150-1000 \ \mu m)$. In contrast, in the high pressure regime, where the corresponding mean free path length of about 27 μ m is much smaller, such kind of backscattering of CO₂ molecules and diffusive influent of CO2 molecules becomes more probable and has to be taken into account. For capillary positions above the central areas of the Pt microstructures, the additional contributions from influent CO₂ are at least partly accounted for in the calibration of the MC simulated signals (see Sec. III C 1). For positions closer to the edges of the microstructures and at low capillary tip heights, the neglect of contributions from areas outside the active Pt field (see Sec. III D) results in a steeper decay of the simulated signal than observed experimentally. Unfortunately, an extension of the MC simulations to include molecule trajectories outside the capillary plane (in order to account for such



FIG. 6. Comparison of measured line scans above a square Pt microstructure (800×800 μ m²) at 3.7 mbar (solid symbols, capillary heights 14, 65, 108, 213, 353, 623, and 973 μ m) and (a) the corresponding simulated line scans obtained by Monte Carlo simulations and by superposition of (b) the gas distribution from point sources, using capillary heights of 20, 40, 80, 150, 350, 700, and 1000 μ m (open symbols). The inset shows the corresponding evolution of the signal intensity (simulation vs measurement) above the center of the Pt fields. Note that additional experimental data points were used which are not shown in the line scans.

events) would considerably increase the computation time in the MC simulations, especially for the high pressure regime, and was therefore not included.

For comparison and in order to gain further information on the deviations in the MC simulations, apart from the calculations presented above, we also calculated the CO₂ product distribution above a Pt microstructure by superposition of the gas distribution above the different Pt surface elements, which are considered here as point sources [see Fig. 1(b)]. The steady-state CO₂ partial pressure N(CO₂) at a position p above the substrate is calculated by adding all contributions from the different surface elements *i*, assuming a quadratic decay of the initial CO₂ concentration above each of the respective elements *i* (element area: $10 \times 10 \ \mu m^2$)

$$N(CO_2) = \sum_i n_i^0 \cdot \frac{c^2}{d_i^2 + c^2}.$$
 (2)

The constant n_i^0 represents the CO₂ concentration directly above the respective element *i*, which for simplicity is assumed to be identical for all elements (no consideration of spatial variations in the activity, as introduced, e.g., by shadowing effects), *c* is the decay constant and describes the distance at which the concentration reaches the value $n_i^0/2$, and *d* describes the distance from the respective surface element *i* to the point p. A fit of the parameters n_i^0 and *c* to the measured data, optimizing the agreement above the central



FIG. 7. Simulation of the CO₂ signal intensity above the central position of a square Pt field $(800 \times 800 \ \mu m^2)$ vs the height of the capillary at different pressures and for varying reaction orders *n* (*n*=0–0.5, see legend). For comparison, a MC simulation using noncorrected parameters (no CFD based corrections) is included as well (black data set).

area of the microstructure, leads to the set of line scans shown in Fig. 6(b). Comparison with the measured data (solid symbols) shows that this model gives a rather good account of the distance dependence of the CO₂ signal above the center of the microstructure. Also, the general shape of the line scans, in particular their characteristic slope at the edge of the microstructure [see Fig. 6(b)], fits rather well to the experimental data for not too small capillary heights, above 80 μ m. For a capillary height of 80 μ m and lower, the simulated CO₂ signals show an increasingly more pronounced smear-out of the decay at the edge of the line scans than the experimental data. Hence, this description, which neglects the effect introduced by the capillary wall, the finite extension of the orifice, and nondiffusive effects on small length scales, results in deviations from the experimental data which are opposite to those in the ballistic model, where the simulated slopes become steeper for close distances than the experimental ones.

In total, a quantitatively correct description of the experimental data at close capillary heights, which yield the best lateral resolution, is not possible by the above superposition model, and also the description by the present ballistic MC simulation is limited under these conditions. More complex extensions of the latter method have to be considered for that purpose.

3. Influence of the flow field on the simulations

In order to compare the influence of the flow field on the MC simulations in the two pressure regimes (0.37 and 3.7 mbar), we also performed MC simulations which do not include the modifications in the local pressure, temperature, and velocity components of the gas molecules determined in the CFD calculations. Furthermore, the influence of different reaction orders was tested using the CFD corrected local parameters in the MC simulations. Figure 7 shows plots of the simulated CO₂ signal (in arbitrary units) above the center of a square Pt microstructure versus the capillary height, concentrating on small capillary heights below 45 μ m. First of all, the reaction order plays an important role on the distance dependence of the CO₂ signal at small heights for increasing total reaction orders. This can be understood from the

effect of the local reactant partial pressure on the local product formation rate. Second, we consider the special case of n=0, where the influence of the reactant partial pressure on the product formation rate disappears and where deviations compared to calculations which do not consider the variations in the flow field parameters determined by the CFD calculations would be solely due to the direct influence of the molecular flow field underneath the capillary (velocity components pointing toward the orifice, increased mean free path due to the pressure drop under the capillary). In this case, we find distinctly higher CO₂ signals for capillary heights below 10 μ m in the high pressure regime (upper data set in Fig. 7). In contrast, the data points show almost no deviation from the results without CFD in the low pressure regime (lower data set). The difference can be explained, on the one hand, by the higher number of collisions in the high pressure regime, resulting in a more effective transfer of momentum from the gas phase molecules to the CO₂ product molecules and, on the other hand, by a favored motion of the CO_2 molecules toward the region underneath the capillary orifice driven by the radial increase of pressure under the capillary tip. Thus, considering the reduction of the molecular flow by the capillary tip becomes important for properly modeling the spatial product gas distribution at very small capillarysample distances (<20 μ m) and, in particular, in the case of high total reaction orders of the catalytic reaction studied.

D. Influence of the capillary-sample configuration

A comparison of the two data sets in Fig. 7 shows that the total signal increases by a factor of about 1.4 in the high pressure regime, independent of the flow field and of the reaction order. To study the physical origin of this difference, the positions of the original desorption elements of the CO_2 molecules hitting the capillary orifice were evaluated. Figure 8(a) shows MC simulations (upper part: 0.37 mbar, lower part: 3.7 mbar) evaluating the fraction of CO₂ molecules that will finally reach the capillary orifice and contribute to the CO_2 mass spectrometry signal, depending on the radial start position on the catalytically active field (surface element) with respect to the center of the capillary tip [cf., Fig. 1(b)]. These MC simulations were performed without considering the influence of the flow field. The insets in both of the graphs exemplarily show the respective two-dimensional maps of the spatial origin of the CO₂ product molecules for a (very low) capillary height of 2 μ m. As expected, the number of "detected" CO₂ molecules originating from the area directly underneath the capillary orifice is almost identical for both pressure regimes for very small capillary heights (below 20 μ m). In the high pressure regime (lower part), however, CO₂ product molecules coming from the region underneath the capillary wall contribute stronger to the CO₂ signal. This tendency is also observed for larger capillary heights, although the relative contribution from the region directly underneath the capillary orifice is considerably smaller in the high pressure regime. Due to the small mean free path of the CO₂ molecules compared to the distance between capillary tip and sample surface, the high number of collisions with gas phase molecules (here, O2 molecules) re-



FIG. 8. (a) Number of CO₂ molecules hitting the orifice of a capillary ($d = 70 \ \mu m$) positioned above the center of a square Pt field (800 $\times 800 \ \mu m^2$) as a function of the radial position of their origin on the sample surface (r=0 at the center of the capillary), both for the low pressure regime (upper panel) and the high pressure regime (lower panel). (b) Normalized volume integral of the radial distribution of the data presented in the lower panel of (a), representing the fraction of CO₂ product molecules originating from the inside of a circular area under the capillary tip with the radius r as a function of the respective radius.

sults in a change of the angular desorption characteristics from a cosine-type distribution to an isotropic distribution. In the case of small capillary heights, the increasing number of collisions in the high pressure regime (gas-gas and gassurface collisions) hinders the motion of CO_2 molecules toward the outer edge of the capillary wall and the molecules desorbing underneath the capillary wall have a higher probability of finally contributing to the overall signal compared to the low pressure regime, independently of the flow field or the reaction order of the respective catalytic reaction.

To highlight the important contribution of the active area underneath the capillary wall to the product signal in SMS measurements in the high pressure regime, we calculated the normalized volume integral of the radial distribution of product desorption events displayed in the lower graph of Fig. 8(a) (p=3.7 mbar). This value, which describes the fraction of the CO₂ signal originating from CO₂ molecules that have desorbed inside of an area on the sample determined by its respective radius (=distance from the center of the orifice), is plotted as a function of radius and for different heights of the capillary in Fig. 8(b). Even for very small capillary heights (below 20 μ m), the percentage of molecules stemming from the area directly underneath the capillary orifice (radius = 35 μ m) is only 15% of the total CO₂ signal and a fraction of 50% is reached only at a radius of about 75 μ m. On the other side, the area contributing mostly to the total CO₂ signal is mainly restricted to the region underneath the tip (orifice plus capillary wall; see insets of Fig. 8), at least for tip heights of 80 μ m and below, i.e., for tip heights, which are significantly lower than the total diameter of the capillary tip. Only for larger capillary heights, catalytically active surface areas outside the capillary projection contribute increasingly to the product signal.

Moreover, the perturbations caused by the presence of the capillary tip at small capillary heights become even more pronounced if the shadowing effects evaluated in the CFD calculations are considered. In this case, the reaction rate in the center of the capillary decreases, resulting in a smaller local CO_2 production, and the molecular flow field pushes product gas species from the region under the capillary wall toward the orifice and thus decreases the lateral resolution of the measurement. This effect has to be considered especially when studying catalytic reactions with a higher reaction order and/or at high pressures.

IV. CONCLUSIONS

Employing a combination of scanning mass spectrometry measurements, Monte Carlo simulations, and CFD calculations, we have analyzed the spatial evolution of CO₂ product molecules above catalytically active Pt microstructures of different size and geometry and at different pressures during continuous CO oxidation. These measurements and calculations, which were performed at length scales and under reaction conditions not easily accessible by conventional modeling packages, provided detailed insight into the gas transport during chemical reaction in the region between sample surface and capillary tip, which is a precondition for the interpretation of data measured on microstructured model catalysts, e.g., for catalyst screening. Furthermore, they illustrate the effects induced by the presence of the capillary probe (shadowing effects) and thus allow us to define measurement and reaction parameter ranges where these effects are negligible ("minimal invasive conditions"). Specifically, the work led to the following conclusions:

(1) Both in the low pressure regime (here around 0.37 mbar), where on the length scales of the sample-probe separation the motion of product gas molecules is dominated by ballistic mass transport, and in the high pressure regime (here, around 3.7 mbar), where collisions with gas phase molecules become increasingly important, shadowing of the educt gases by the capillary results in an increasingly serious pressure drop within the gap between capillary tip (\emptyset =300 µm) and sample surface for very small capillary heights (below 20 µm). Moreover, in the high pressure regime, the flow of reactant gas molecules directed toward the orifice of the probing capillary tip pushes CO₂ molecules

from the region underneath the capillary wall toward the orifice and thus lowers the lateral resolution.

- (2) Due to the shadowing of educt gases, the reaction rate in the region underneath the capillary is lowered, with the extent depending on the total reaction order and the actual reaction conditions. Especially for catalytic reactions with higher total reaction orders, the distance between sample and capillary tip has to be large enough to avoid severe effects on the reaction process.
- (3) Generally, a well-defined capillary tip geometry with a very thin capillary wall is desirable to obtain high lateral resolution and minimize perturbations of the catalytic reaction process. However, although scaling down of the capillary orifice can be easily achieved in combination with the reduction of the length of the capillary channel to maintain similar flow rates,³⁰ it is only worthwhile if accompanied by a reduction of the capillary wall thickness.
- (4) At higher pressures, backscattering of product molecules which initially missed the orifice of the capillary results in an accumulation of product gas species around catalytically active sample areas, which complicates a quantitative evaluation of the spatial gas evolution and lowers the spatial resolution.

The good agreement between measurements and the combination of Monte Carlo simulations achieved in the low pressure regime shows that under these conditions, with pressures below 1 mbar and capillary heights below a critical value of approximately 80 μ m (below the diameter of the capillary orifice), the spatial distribution of product gas species measured by the finite size capillary can be unambiguously related to desorption processes at locations on the sample surface underneath the orifice. At higher pressures, effects caused by multiple collisions with the flow field of reactant molecules streaming toward the orifice of the capillary and backscattering of molecules become increasingly important and have to be considered, e.g., by CFD calculations. Also under these conditions, however, reasonable agreement between experimental and simulated data can be reached. In total, the data provide an excellent basis for analysis of catalyst reactivities in microstructured model systems.

ACKNOWLEDGMENTS

We are indebted to C. Pfahler (Institute of Solid State Physics, Ulm University) for producing the microstructured samples. Financial support by the Deutsche Forschungsgemeinschaft (DFG) within the Collaborative Research Center (SFB) 569 is gratefully acknowledged.

- ¹B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, and W. H. Weinberg, Angew. Chem. **111**, 2648 (1999).
- ²S. Senkan, Angew. Chem., Int. Ed. 40, 312 (2001).
- ³S. Senkan, K. Krantz, S. Ozturk, V. Zengin, and I. Onal, Angew. Chem., Int. Ed. **38**, 2794 (1999).
- ⁴M. Orschel, J. Klein, H.-W. Schmidt, and W. Maier, Angew. Chem., Int. Ed. **38**, 2791 (1999).
- ⁵J. Urschey, P. A. W. Weiss, J. Scheidmann, R. Richter, and W. F. Maier,
- Solid State Sci. 5, 909 (2003). ⁶D. Farrusseng, Surf. Sci. Rep. 63, 487 (2008).

- ⁷ B. Weidenhof, M. Reiser, K. Stöwe, W. F. Maier, M. Kim, J. Azurdia, E. Gulari, E. Seker, A. Barks, and R. M. Laine, J. Am. Chem. Soc. 131, 9207 (2009).
- ⁸K. Eckhard, O. Schlüter, V. Hagen, B. Wehner, T. Erichsen, W. Schuhmann, and M. Muhler, Appl. Catal., A 281, 115 (2005).
- ⁹ P. Cong, R. D. Doolen, Q. Fan, D. M. Giaquinta, S. Guan, E. W. McFarland, D. M. Poojary, K. Self, H. W. Turner, and W. H. Weinberg, Angew. Chem., Int. Ed. **38**, 483 (1999).
- ¹⁰ M. Johansson, I. Lundström, and L.-G. Ekedahl, Rev. Sci. Instrum. 71, 3513 (2000).
- ¹¹ M. Johansson, J. Hoffmann Jørgensen, and I. Chorkendorff, Rev. Sci. Instrum. 75, 2082 (2004).
- ¹²N. Li, K. Eckhard, J. Assmann, V. Hagen, H. Otto, X. Chen, W. Schuhmann, and M. Muhler, Rev. Sci. Instrum. 77, 084102 (2006).
- ¹³ M. Johansson, O. Lytken, and I. Chorkendorff, Surf. Sci. **602**, 1863 (2008).
- ¹⁴ J.-S. Choi, W. P. Partridge, and C. S. Daw, Appl. Catal., A 293, 24 (2005).
- ¹⁵ R. Horn, N. J. Degenstein, K. A. Williams, and L. D. Schmidt, Catal. Lett. **110**, 169 (2006).
- ¹⁶ R. Horn, K. A. Williams, N. J. Degenstein, and L. D. Schmidt, J. Catal. 242, 92 (2006).

- ¹⁷R. Horn, K. A. Williams, N. J. Degenstein, A. Bitsch-Larsen, D. D. Nogare, S. A. Tupy, and L. D. Schmidt, J. Catal. **249**, 380 (2007).
- ¹⁸ A. Bitsch-Larsen, K. L. Howard, and L. D. Schmidt, Appl. Catal., A 348, 165 (2008).
- ¹⁹A. Bitsch-Larsen, N. J. Degenstein, and L. D. Schmidt, Appl. Catal., B 78, 364 (2008).
- ²⁰ A. Urakawa and A. Baiker, Top. Catal. **52**, 1312 (2009).
- ²¹S. Kielbassa, M. Kinne, and R. J. Behm, Langmuir 20, 6644 (2004).
- ²² M. Roos, S. Kielbassa, C. Schirling, T. Häring, J. Bansmann, and R. J. Behm, Rev. Sci. Instrum. 78, 084104 (2007).
- ²³ M. Johansson, T. Johannessen, J. Hoffmann Jørgensen, and I. Chorkendorff, Appl. Surf. Sci. 252, 3673 (2006).
- ²⁴T. Matsushima, Surf. Sci. **127**, 403 (1983).
- ²⁵M. U. Kislyuk and T. N. Bakuleva, Russ. Chem. Bull. 39, 2446 (1990).
- ²⁶G. Cao, Y. Seimiya, Y. Ohno, and T. Matsushima, Chem. Phys. Lett. **294**, 419 (1998).
- ²⁷I. Rzeźnicka and M. G. Moula, J. Chem. Phys. **119**, 9829 (2003).
- ²⁸ Y.-F. Y. Yao, J. Catal. 87, 152 (1984).
- ²⁹ P. J. Berlowitz, C. H. F. Peden, and D. W. Goodman, J. Phys. Chem. 92, 5213 (1988).
- ³⁰B. Kasemo, Rev. Sci. Instrum. 50, 1602 (1979).