CO Oxidation on Stepped Rh Surfaces: μm -Scale Versus Nanoscale

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Abstract

The catalytic CO oxidation reaction on stepped Rh surfaces in the 10^{-6} mbar pressure range was studied in situ on individual μm -sized high-Miller-index domains of a polycrystalline Rh foil and on nm-sized facets of a Rh tip, employing photoemission electron microscopy (PEEM) and field-ion/field-emission microscopy (FIM/FEM), respectively. Such approach permits a direct comparison of the reaction kinetics for crystallographically different regions under identical reaction conditions. The catalytic activity of the different Rh surfaces, particularly their tolerance towards poisoning by CO, was found to be strongly dependent on the density of steps and defects, as well as on the size (μm vs. nm) of the respective catalytically active surface.

Graphic Abstract

Keywords Surface reaction kinetics · PEEM · FEM/FIM · CO oxidation · Rhodium

1 Introduction

The catalytic properties of precious metal nanoparticles strongly depend on their size, shape and the atomic arrangement of their confining surfaces. For example, for *fcc* metals

such as Pt, Pd, or Rh, systematic studies of structure–function relations using single crystals as model catalysts have shown that the high-Miller-index planes, i.e. open-structure surfaces, exhibit higher catalytic activity than low-index planes, consisting of densely packed atoms [1–3]. This is due to the abundance of low-coordinated metal atoms which facilitate the interaction with reacting molecules and are active sites for breaking/making chemical bonds [3–6]. Additionally, some stepped high-Miller-index *fcc* surfaces exhibit higher thermal and chemical stability both under reducing and oxidizing conditions [3, 7]. Recently it was demonstrated that surface steps may not only be particularly

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active sites, but they also influence the stability of the catalytically active state and can modulate kinetic oscillations [8, 9]. Therefore, metal nanoparticles with high-Miller-index facets are beneficial for catalytic applications, but their synthesis is a challenging task, considering the energetics of crystal growth favouring low-index planes [10–12]. However, in order to learn which facets enclosing the designed particles are worth striving for, one needs to study catalytic reactions on high-Miller-index facets, so that the most active facets could be identified.

Usually, such studies are performed on flat single crystal surfaces cut to different high-Miller-index orientations [13, 14], or on curved crystals with the step density varying across the sample surface [15–18]. The first approach requires performing separate experiments for several differently oriented surfaces, but keeping experimental parameters such as pressure and temperature identical in different experiments is sometimes difficult. The second approach of using curved surfaces, when combined with spatially-resolved X-ray photoelectron spectroscopy (XPS), allows analysis of the surface composition on a μm -scale and can be even extended to near ambient pressure (NAP-XPS [18]). Nevertheless, extracting local kinetic data from gas-phase NAP-XPS spectra or local sampling of reaction products by scanning micrometer-size “sniffer” mass spectroscopy (MS) [19] suffers from the obstacle that different surface regions can not be probed *simultaneously* (scanning working principle) and that reaction products from neighbouring surfaces sites can not be fully excluded.

In the present contribution, as an alternative approach we apply a *surface structure library* [9, 20], i.e. a sample containing adjacent regions with different, but crystallographically well-defined orientations. Polycrystalline metal foils, consisting of many adjacent μm -sized differently oriented domains separated by grain boundaries are, e.g. proper candidates. By determination of crystallographic orientation of the individual domains using electron backscatter diffraction (EBSD) such foils turn into real well-defined surface structure libraries [8, 9, 20, 21]. Since the crystalline grains are in the 10–300 μm range, hundreds of individual domains with dozens of different orientations can be found on a $1 \times 1 \text{ cm}^2$ foil.

In an experiment, all different domains are “naturally” exposed to the very same pressure/temperature conditions, so a direct comparison of different crystallographic orientations is straightforward. An ongoing catalytic reaction is visualized in real time by PEEM and the digital analysis of the in situ recorded PEEM video-files provides the required spatially-resolved kinetic information (*kinetics by imaging* [22]). A series of CO and H_2 oxidation studies on individual μm -sized low Miller index Pt and Pd domains, as well as on supported Pd particles, demonstrated the applicability and reliability of this approach [21–26].

Herein, we apply the same approach and the same polycrystalline Rh sample as in our recent study of H_2 oxidation

on stepped Rh surfaces [26], but for CO oxidation, a reaction that has been extensively studied on platinum group metals due to its importance in automobile exhaust gases treatment. For rhodium, renewed interest is due to increasingly using Rh for the newest generation of automotive catalytic converters designed for direct injection gasoline engines working under lean-burn conditions (e.g. “four way catalyst” by BASF [27]) and for purification of the hydrogen feed of proton-exchange membrane fuel cells [28]. Previous CO oxidation studies on Rh are mostly focused on low-index surfaces [29–32] whereas data for high-Miller-index Rh surfaces are scarce. Accordingly, we analyze and compare the reaction kinetics on individual μm -sized highly stepped high-Miller-index Rh domains exhibiting different step density and different terrace orientation between the steps.

For an analogous study on the nm-scale, the apex of a Rh nanotip, exhibiting a very high curvature, was used to model an individual catalytic nanoparticle with a highly stepped surface, similar, e.g. to particles recently analysed by molecular dynamics [33] or earlier by electron microscopy [34, 35]. Like a nanoparticle, such a nanotip exhibits differently oriented nano-facets, but in contrast to a technological catalyst nanoparticle, the nanotip surface can be prepared in a controlled way by field evaporation and characterised by field-ion microscopy (FIM) with atomic resolution. Switching to the field-electron (FEM) imaging mode (just by reversing the tip-voltage polarity) CO oxidation on such a well-defined nanosized sample can be imaged in situ on the nanoscale [36, 37].

2 Experimental

The experiments were performed in two different all-metal UHV setups: (i) a PEEM/XPS setup consisting of separate PEEM and XPS chambers that are connected by a UHV sample transfer line and (ii) a FIM/FEM setup that can be operated either in the FIM mode, using Ne as the imaging gas, or in the FEM mode.

The PEEM/XPS setup is equipped with a PEEM (Staib Instruments), a deuterium discharge UV lamp (photon energy $\sim 6.5 \text{ eV}$) for electron excitation, a mass spectrometer (MKS Instruments), an XPS system (Phoibos 100 hemispherical energy analyzer and XR 50 twin anode X-ray source, both from SPECS), a high purity gas supply system (O_2 : 99.99%, CO : 99.98%) and sample preparation facilities for cleaning the sample by argon ion sputtering and subsequent annealing.

For catalytic studies, the PEEM chamber was operated as a flow reactor for CO oxidation on a polycrystalline Rh foil, with the reaction visualized in situ by PEEM and image recording by a CCD camera (Hamamatsu). The sample consisted of a $10 \times 12 \text{ mm}^2$ polished polycrystalline

Fig. 1 Surface structure library of stepped Rh surfaces: **a** a 550 μm wide sector of a clean polycrystalline Rh foil consisting of μm -sized differently oriented high-Miller-index domains as imaged by PEEM; **b** optical image of the same field of view; **c** EBSD color-coded map

of the same region with crystallographic orientations of individual domains indicated. The inverse pole figure is shown for reference in the bottom right corner. Figure 1c is taken from Ref. [26]

Rh foil of 0.2 mm thickness (Mateck, 99.99%) which was cleaned in UHV by repeated cycles of sputtering with Ar^+ ions at 1 keV at 300 K and consecutive annealing to 973–1073 K for 30 min. The sample temperature was measured by a Ni/NiCr thermocouple spot-welded directly to the sample. The cleanliness of the sample was confirmed by XPS before each experiment. The PEEM magnification, sufficient for monitoring the ongoing reaction on individual μm -sized domains of the polycrystalline sample (Fig. 1a), was calibrated by comparison of PEEM images with optical micrographs of the same Rh foil (Fig. 1b).

To study the processes on individual μm -sized domains of a polycrystalline foil, their exact crystallographic orientation must be determined first. For the present study, a Rh sample already previously characterized and used for H_2 oxidation [8, 9] was employed (Fig. 1c).

Details of the EBSD measurements in a field emission scanning electron microscope (FEI Quanta 200F) and the evaluation procedures were described in the SI of Ref. [8] and in Ref. [9]. The EBSD map in Fig. 1c (same field of view as in Fig. 1a) contains the crystallographic orientations and the inverse pole figure.

The nanoscale studies were performed in a FIM/FEM setup containing a specimen holder enabling exact temperature control from 78 to 900 K and a channel-plate/screen assembly for imaging by ions of noble (Ne) or reactive (H_2 , O_2) gases (in the FIM mode) or by electrons (in the FEM mode), respectively. The FIM/FEM chamber was equipped with the same MS and a similar gas supply system (for reactive gases and Ne) as the PEEM setup.

Similarly as for the Rh foil by PEEM, for catalytic studies on the Rh nanotip the FIM/FEM chamber was operated as a flow reactor, whereas FEM was used as a reaction imaging tool (resolution ~ 2 nm). The Rh nanotip (the same as was used in our recent study of H_2 oxidation [26]) was fabricated by electrochemical etching of a Rh wire (0.1 mm, Mateck, 99.99%) followed by field evaporation at 77 K in UHV for fine shaping and cleaning of the surface under Ne^+ FIM imaging control (with atomic resolution). The temperature of the tip was measured by a Ni/NiCr thermocouple spot-welded to its shank. The FIM images during the tip preparation and the FEM images during the ongoing CO oxidation were recorded with an identical camera as in the PEEM experiments. In Fig. 2a the FEM image of the clean

Fig. 2 The apex of a Rh nanotip serves as a model of a Rh nanoparticle. **a** FEM image of the [111]-oriented Rh nanotip; **b** the same but imaged by FIM using Ne^+ ions (taken from [26]); **c** 3D ball model

based on the atomically resolved FIM images. Atoms visible in the FIM micrograph are marked in green

Rh nanotip is shown; in Fig. 2b the corresponding FIM image is displayed, obtained with Ne^+ ions at 77 K and at an applied field of 35 V/nm. Figure 2c presents a realistic 3D model of the tip apex, constructed on the basis of the atomically resolved FIM images. Surface atoms, visible in the FIM micrograph (Fig. 2b), are marked green in Fig. 2c (only protruding atoms are imaged by FIM, due to the local field based FIM imaging mechanism [37, 38]).

3 Results and Discussion

3.1 Individual μm -Sized Rh Domains

Catalytic CO oxidation on Rh may exhibit kinetic bistability, understood as existence of two different stable steady states at the same set of external parameters, over a wide range of parameters [39]. Solely the system prehistory determines which of the two steady states (high or low catalytic activity) prevails: the high activity state is accessed from the oxygen excess regime, whereas the inactive state is reached from the CO excess regime. The bistable behaviour of CO oxidation is a result of the different adsorption kinetics of CO and O_2 , as CO inhibits the (dissociative) adsorption of oxygen, but not vice versa [39, 40]. The bistability shows up as a hysteresis of the reaction rate upon cyclic variation of control parameters, e.g. the CO pressure (at constant p_{O_2} and T) [21–24]. Figure 3 illustrates this behaviour for the present case of polycrystalline Rh: at a reaction temperature of 393 K, the sample was exposed to a constant oxygen partial pressure (1.0×10^{-6} mbar) while the CO partial pressure (p_{CO}) was swept up and down with the CO_2 production rate (R_{CO_2}) simultaneously monitored by mass spectrometry (Fig. 3b). At low CO pressures, the Rh surface is oxygen covered and increasing the CO pressure leads to an increased R_{CO_2} until a kinetic phase transition occurs at $p_{\text{CO}} = \tau_A$, manifested by a drop in R_{CO_2} . It is caused by the sudden loss of catalytic activity due to switching from the oxygen covered to the CO covered surface (the latter detectable by its darker contrast in PEEM than the oxygen covered surface). When subsequently decreasing p_{CO} , the Rh surface remains in the CO poisoned (low activity) steady state until a second kinetic transition (re-establishing of the O covered surface) takes place at $p_{\text{CO}} = \tau_B$. Such hysteresis behaviour is typical for the Langmuir–Hinshelwood mechanism of CO oxidation on platinum group metals [21–24, 39–41].

Our previous studies on Pt and Pd revealed that the position of the bistable region in the parameter space is very sensitive to the surface structure [21–24]. In the present work we make use of this effect to measure differences in reaction kinetics on crystallographically different high-Miller-index Rh surfaces. For this, we visualize the reaction in situ by PEEM and video-monitor it in parallel to the MS measurements shown in Fig. 3b.

Fig. 3 Catalytic CO oxidation on Rh: **a** PEEM image illustrating the PEEM contrast during CO oxidation (the same field of view as in Fig. 1a): the left hand half shows oxygen covered Rh surface, the right hand half the CO covered surface (always darker contrast in comparison to the same, but oxygen covered surface). The Rh(7 $\bar{1}$ 8) and Rh(5 5 3 1) domains are contoured by green and red lines, correspondingly; **b** hysteresis in the global CO_2 production rate as measured by MS during cyclewise variation of the CO pressure at constant $p_{\text{O}_2} = 1.0 \times 10^{-6}$ mbar and 393 K; **c** PEEM video-frames taken during the kinetic transition τ_A . The frames correspond to the square region (dashed line) on the Rh(7 $\bar{1}$ 8) domain in (a). Frame 1: oxygen covered surface; frame 2: during the kinetic transition τ_A ; frame 2*: the same as frame 2, but color-coded instead of grey scale. The correspondence of grey scale and color code is shown on the left of frames 1 and 2*; frame 3: CO covered surface; **d** hysteresis in the local PEEM intensity measured within ROI1 (green square within Rh(7 $\bar{1}$ 8) domain). The numbered positions on the hysteresis curve correspond to the frame numbers in (c); **e** the same but for Rh(5 5 3 1), ROI2 is marked as red square in (a)

In contrary to MS, which per se averages R_{CO_2} over the entire sample, PEEM is a spatially resolving technique: photoelectrons emitted from the UV illuminated surface provide simultaneous information about each region in the field of view with a resolution of $\sim 1 \mu\text{m}$ (for our setup; up to 15 nm for newest PEEM design [42]). The local intensity of the PEEM image depends on the local work function and thus on the surface concentration of adsorbed reactants. Since the reaction rate depends on the concentration of adsorbates as well, the image intensity reflects the reaction rate, at least for reactions following the Langmuir–Hinshelwood mechanism. In this way spatially-resolved reaction kinetics for individual Rh(hkl) domains can be extracted by the local intensity analysis of PEEM images (*kinetics by imaging* [22], for applications see Refs. [8, 9, 21, 23–26]). Such measurements are

comparable to scanning micrometer-size “sniffer” MS [19], but without the drawbacks mentioned above.

Figure 3c–e present examples of spatially resolved PEEM measurements for the Rh(7 $\bar{1}$ 8) and Rh(5 $\bar{5}$ 3 11) domains. Figure 3c shows PEEM video frames (magnified square region marked in Fig. 3a) taken during a kinetic transition τ_A (cf. the parallel MS measurement in Fig. 3b). The corresponding hysteresis curve of the local PEEM image intensity of a square ROI ($15 \times 15 \mu\text{m}^2$) located within the Rh(7 $\bar{1}$ 8) domain is shown in Fig. 3d. Figure 3e shows the analogous local PEEM intensity measured within the Rh(5 $\bar{5}$ 3 11) domain. A direct comparison of τ_A and τ_B positions for Rh(7 $\bar{1}$ 8) and Rh(5 $\bar{5}$ 3 11) proves the structure dependence of CO oxidation on Rh (compare Fig. 3d, e), in contrast to the widespread opinion of structure insensitive CO oxidation on Rh (see [43] and references therein).

An interesting feature of the observed kinetic transitions is the formation of cellular-like structures (frame 2 in Fig. 3c and the same image, but color-coded, as frame 2* for better visibility): small short-living dark gray islands nucleate creating a fluctuating turbulent picture during the kinetic transition. These structures formally resemble the patterns observed by Rose et al. during CO oxidation on Pt(110) by mirror electron microscopy (MEM) [44], but they differ by much faster temporal evolution (tens of μs in the present case vs. few s in Ref. [44]). Unfortunately, the spatial resolution of our PEEM (lower μm range) which is much worse than that of MEM used in the study [44] prevents a discussion of the development of the size, shape or density of the observed fluctuating structures. The authors of [44] associated the observed cellular structures with the formation of CO islands on Pt(110), which seems to be in accordance with the present observations. Indeed, on Pt(110) cellular-like structures were visible in regions containing step-bunches and also our surface is a high-Miller-index stepped surface. This interpretation is also in agreement with a previous nanoscale study by some of us [45], in which a drastical increase in the correlation length of reaction-induced fluctuations and therefore also in the size of nucleating CO islands (from nm to μm scale) was predicted for certain conditions in the bistable range of the reaction. Based on the current observations, performed at the limit of the spatial and temporal resolution of the employed PEEM, one can not judge whether the formation of the observed short living cellular patterns is related to this effect. As alternative explanation, the combination of possible microscopic reaction-induced roughening (as observed for Pt(110) in [46]) and the varying substrate dependent binding sites of CO influencing the spatial pattern formation (e.g. Pd vs. Rh, [47]), may contribute to the observed phenomenon.

In variance to the mesoscopic reaction fronts, often observed during CO oxidation on low index Pt and Pd surfaces [21, 23, 24, 47], such fronts were not observed here.

To our knowledge, mesoscopic fronts were not yet directly observed during CO oxidation on Rh under high vacuum conditions. Microscopic fronts, however, were observed by STM in titration experiments on Rh(110) [48].

Varying the reaction temperature at constant p_{O_2} alters the positions of the transitions τ_A and τ_B . Plotting the τ_A and τ_B pressures versus the reciprocal temperature, a *kinetic phase diagram* can be constructed, in which the steady state regions and the region of bistability are marked. Such diagrams appeared to be particularly helpful in revealing and understanding mechanisms of reactions in homogeneous phase such as the Briggs-Rauscher (BR) or Belousov-Zhabotinsky (BZ) oscillating reaction [49, 50] and have also been applied to heterogeneous systems such as $(\text{CO} + \text{O}_2)/\text{Me}$ [51, 52] or $(\text{H}_2 + \text{O}_2)/\text{Me}$ [53] for many years. The analogy to equilibrium thermodynamics justifies the use of the term “phase diagram”: as noticed already by Schlögl in the 1970s, the cooperative phenomena play a crucial role in both, equilibrium and nonequilibrium phase transitions, forming, e.g. ordered structures in an equilibrium, and

Fig. 4 CO oxidation on differently oriented high-Miller-index Rh surfaces: **a** kinetic phase diagrams for individual domains visible in the PEEM field of view (cf. Fig. 1c); **b** surface structures corresponding to particular Rh(hkl) domains; **c** position of the kinetic transition τ_A in dependence of the average number of nearest neighbours

selforganizing dissipative structures in a nonequilibrium situation [54–56]. From this point of view, the appearance of instabilities, kinetic transitions or kinetic oscillations can be treated as the appearance of different competitive reactive “phases” [57]. Figure 4a shows such diagrams for different stepped Rh(hkl) domains visible in the field of view in Fig. 3a for constant O_2 pressure of 1.0×10^{-6} mbar and for a temperature interval of 393–458 K.

The analysis of the diagrams in Fig. 4 shows that various structural factors such as the density of steps (related to the width of the terraces), the structure of terraces and the shape of the steps influence the relative position of a diagram. In an attempt to find a common descriptor, these factors can be traced back to an average nearest neighbours number, representing a simple quantitative approximation. For illustration, the position of kinetic transition τ_A which reflects the tolerance of the system towards CO poisoning can be plotted versus the average nearest neighbours number. Figure 4c convincingly shows the resulting correlation for an exemplary temperature of 413 K: the lower the average coordination of surface atoms is, the higher is the CO pressure necessary to poison the surface, i.e. the rougher surfaces are the “better” catalysts.

3.2 Stepped Surfaces of a nm-Sized Rh Tip

To directly compare the μ m- and nm-scale behaviour of CO oxidation on stepped Rh surfaces, the reaction was also studied by FEM using the same Rh nanotip that was used in our recent study of H_2 oxidation [26]. The FIM pictures with atomic resolution (Fig. 2b), taken at different applied fields, allowed us to construct an improved ball model (Fig. 2c).

Catalytic experiments were performed in the same manner and under the same conditions as for the polycrystalline Rh foil. Figure 5a shows FEM video frames illustrating the kinetic transitions τ_A and τ_B during the cyclewise variation of the CO pressure at constant O_2 pressure (1.0×10^{-6} mbar) and temperature (403 K). Again, alike PEEM, the bright contrast corresponds to the high activity state and dark contrast to the low activity state. The corresponding hysteresis loop and the resulting kinetic phase diagram are shown in Fig. 5b, c.

3.3 Comparison of μ m-Sized and nm-Sized Rh Surfaces

Kinetic phase diagrams are not only suitable to compare catalytic behaviour of differently oriented domains of the same sample (as e.g. in Fig. 4a), but also to compare different systems under similar conditions, in the present case a polycrystalline Rh foil and a Rh nanotip. The comparison in Fig. 6 reveals that for the Rh nanotip the diagram is significantly shifted to higher CO pressure (by a factor of ~ 3). This

Fig. 5 CO oxidation on a Rh nanotip: **a** examples of FEM video frames taken during cyclewise variation of the CO pressure at constant oxygen pressure of 1.0×10^{-6} mbar and at constant temperature of 403 K; **b** corresponding hysteresis-like curve of the FEM image intensity; τ_A and τ_B mark the kinetic transitions between the steady states of low and high catalytic activity, the numbers on the curve correspond to the frames in (a); **c** τ_A and τ_B values for different temperatures in the range of 393–453 K and constant oxygen pressure of 1.0×10^{-6} mbar, summarised in a kinetic phase diagram

indicates that reaction inhibition by CO poisoning occurs on the nanotip at a considerably higher CO partial pressure and that the tip surface is also reactivated at a higher CO pressure than the Rh foil. Accordingly, the Rh nanotip is a better CO oxidation catalyst than the Rh foil, both on average but also for each individual μ m-sized high-Miller-index Rh domain.

To rationalize these experimental findings, a Rh foil sample with a step density closer to that of the Rh tip surface was prepared by Ar^+ sputtering (*cf.* our recent STM observation of the Ar^+ created steps and defects on Pd [21]). The phase diagram for such an artificially defected Rh surface is also shifted to higher CO pressures when compared the annealed high-Miller-index Rh domains, but it is still located in between annealed foil and Rh nanotip (Fig. 6). The equivalence of the isobaric and isothermal experiments demonstrated in our previous study [24] allows prediction of the ignition and extinction temperatures from kinetic phase diagrams as schematically shown in Fig. 6 (see detailed explanation in Ref. [24]). In the present case this means that corresponding ignition and extinction points are shifted to lower temperatures for the sputtered (more rough) Rh surface with respect to the annealed (more flat) Rh surfaces. This effect already observed earlier for Pd under similar conditions [21] could also be observed under more realistic NAP conditions, where for a stepped Pd surface the ignition/extinction loop was shifted to lower temperatures as compared to smooth Pd(111) [18].

It is known that the binding energy of oxygen at low-coordination defect sites is considerably higher than that on flat terraces of Rh; that is, atomic oxygen binds more

Fig. 6 Comparison of the kinetic phase diagrams for CO oxidation on two individual annealed Rh foil domains (green and red), on the same, but additionally Ar^+ sputtered foil (blue) and on a Rh nanotip (pink). All diagrams were constructed for constant oxygen pressure of 1.0×10^{-6} mbar. Dotted horizontal line at $p_{\text{CO}} = 0.5 \times 10^{-6}$ mbar exemplarily shows the extraction of the predicted ignition and extinction temperatures T_i and T_e

strongly to a defect-rich Rh surface [58, 59]. Although the CO binding energy is also increased on such defect sites [60], the impact on the CO adsorption kinetics seems to be rather small when compared to oxygen. Since the energetics govern the kinetics of the competitive CO and oxygen coadsorption [25], this explains why higher CO pressure is required to poison the surface on sputtered Rh.

Nevertheless, this does not explain the remarkable difference between a sputtered Rh foil and a Rh tip consisting mainly of stepped nano-facets. Apparently, the reaction-induced fluctuations, which have significant effects on kinetic transitions in nm-sized reaction systems [45], shift the whole phase diagram of a Rh nanotip to higher CO pressures. Interestingly, recent studies of catalytic H_2 oxidation have also shown that the Rh nanotip exhibited higher activity than sputtered and annealed Rh foils [26].

Discussing the FEM results, the possible effect of the applied electrostatic field (required for field emission imaging) on the reaction should be mentioned. The applied field values (< 5 V/nm) are comparable with those commonly applied in STM and are far below values which redistribute the electron density near the metal surface [61], and which would influence the interaction of adsorbed molecules with the catalyst surface [62, 63]. Furthermore, in the FEM experiments the tip is negatively charged (in contrary to FIM), and the onset of field emission of electrons is reached far below field values at which electron density modifications occur (see also the according discussion in Ref. [26]). A previous CO oxidation study on Pt using a pulsed high-voltage supply with varying duty pulses provided direct experimental

evidence of this picture and justified to consider the present FEM studies as quasi field-free [64].

4 Summary

Kinetic measurements of CO oxidation on stepped Rh surfaces were performed based on the analysis of microscopic PEEM and FEM video frames, recorded in situ during the ongoing reaction. As catalytic model systems, μm -sized high-Miller-index domains of a polycrystalline Rh foil and the nm-sized facets of the apex of a Rh nanotip were used. The reaction was monitored in the 10^{-6} mbar pressure range by PEEM for the crystalline grains of the Rh foil and by FEM for the Rh tip apex, with the latter characterized at atomic resolution by FIM.

Kinetic phase diagrams for CO oxidation in the 10^{-6} mbar pressure range were constructed for μm -sized stepped Rh surfaces, for the same surfaces but artificially defected by Ar^+ sputtering, and for the stepped surfaces of a Rh nanotip. The comparison of the diagrams for differently structured Rh domains reveals a remarkable structure effect, with factors such as the density of steps (related to the width of the terraces), the structure of terraces and the shape of the steps, influencing the reaction kinetics. An artificially defected Rh surface appeared to be much more tolerant towards CO poisoning than the same, but annealed surface. The nm-sized stepped facets of a Rh nanotip were, however, found to be even more CO tolerant, indicating the existence of a size-effect presumably caused by reaction-induced fluctuations.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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