Cite as: Y. Suchorski *et al.*, *Science* 10.1126/science.abf8107 (2021).

Resolving multifrequential oscillations and nanoscale interfacet communication in single-particle catalysis

Y. Suchorski¹, J. Zeininger¹, S. Buhr¹, M. Raab¹, M. Stöger-Pollach², J. Bernardi², H. Grönbeck³, G. Rupprechter^{*†}

¹Institute of Materials Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria. ²University Service Center for Transmission Electron Microscopy, TU Wien, Wiedner Hauptstraße 8-10, 1040 Vienna, Austria. ³Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, 41296 Göteborg, Sweden.

^{*}Corresponding author. Email: guenther.rupprechter@tuwien.ac.at

In heterogeneous catalysis research, the reactivity of the individual nanofacets of single particle is typically not resolved. We applied in situ field electron microscopy (FEM) to the apex of a curved rhodium crystal (radius of 650 nanometers), providing high spatial (~2 nanometers) and time resolution (~2 ms) of oscillatory catalytic hydrogen oxidation, imaging adsorbed species and reaction fronts on the individual facets. Using ionized water as imaging species, the active sites were directly imaged by field ion microscopy (FIM). The catalytic behavior of differently structured nanofacets and the extent of coupling between them were monitored individually. We observed limited interfacet coupling, entrainment, frequency-locking, and reconstruction-induced collapse of spatial coupling. The experimental results are backed-up by microkinetic modelling of time-dependent oxygen species coverages and oscillation frequencies.

The overall reactivity of a technological catalyst results from the superposition of the activity of a huge number of oxide-supported metal nanoparticles (NPs) that can vary in size, shape and type of exposed facets. Furthermore, the properties of each single NP result from the superposition of its individual facets and their interfaces. In the course of a reaction, the different metal NPs and facets may even respond differently to the reaction conditions, such as through restructuring (1), oxidation (2), coking (3), or sintering (4). All of these effects limit the validity of ensemble-derived structure-performance relations.

Several methods have been used to study the catalytic properties of single catalyst particles, including electron microscopy (5–7), nuclear magnetic resonance (8), Raman, (nano-)infrared (9), X-ray scattering and nanotomography (10, 11), fluorescence (12), and plasmonic nanospectroscopy (13). Our recent studies of individual Pd NPs by photoemission electron microscopy (PEEM), revealed, using the “kinetics by imaging” approach, a long-ranging communication effect of the metal-oxide interface in CO oxidation (14). In this approach, single particle kinetic measurements were based on the local PEEM image intensity variation during the reaction. However, the individual facets of the Pd particles could not be resolved because of the resolution limit of the PEEM used.

Herein, this approach is refined by resolving even the individual (hkl)-nanofacets of a single catalytic particle. We applied in situ field electron microscopy (FEM), which provided

high spatial (~2 nm) and time resolution (~2 ms) and allowed imaging of adsorbed species and reaction fronts, to catalytic hydrogen oxidation on a hemispherical apex of a curved Rh crystal (radius of 650 nm). The FEM studies were complemented by directly visualizing the active sites using the ionized reaction product (H₂O molecules) as imaging species in the field ion microscopy (FIM).

Altogether, we obtained a comprehensive picture of the ongoing oscillatory hydrogen oxidation, visualizing the working surface, reactants, and even the products. Dozens of nanofacets could be individually resolved, revealing their reactivity (active sites) and the nanoscale communication between them during the reaction in real time. Furthermore, we detected how just a few atomic rows on the surface could influence the local activity, leading to frequency-locking and entrainment effects and eventually to a collapse of spatial coupling. The experimental results were supported by microkinetic modelling of time-dependent oxygen coverages and oscillation frequencies.

Like a smaller multifaceted catalytic NP, the curved Rh crystal exhibited several nanometer-sized facets (10 to 100 nm diameter) of different crystallographic orientations (a scanning electron microscopy image is shown in Fig. 1A). The surface of the apex of the Rh specimen could be imaged by FEM (Fig. 1B) allowing monitoring of the facet-resolved kinetics, transfer of species and reaction coupling between facets. In FEM, the electric field applied to the sample deforms the potential barrier on the surface, leading to tunnelling of

electrons into vacuum. The emitted electrons are accelerated toward a screen, where they form a magnified projection image of the surface with ~2 nm resolution.

The image contrast in a FEM results from the local work function convoluted with the local electrostatic field. As a result, FEM allows direct identification of adsorbed reactants on the sample surface, provided the work function differences are large enough for detectable image-contrast. In addition to “static” imaging, FEM can also monitor dynamic surface processes in real time, such as diffusion (15, 16) or catalytic surface reactions (17–20).

The specimens used in previous FEM and FIM studies (17–21) were typically nanotips with a radius of curvature one magnitude smaller (25–50 nm) than the curved crystal of the present study, so that the effects presented herein could not be observed. Catalytic H₂ oxidation is a well-suited reaction for FEM imaging because there is a sufficient work function difference between the catalytically inactive, oxygen-covered Rh surface (high O_{ads} coverage, high work function, and dark contrast) and the active surface (low H_{ads} and O_{ads} coverage; low work function, and bright contrast) (20). Unlike scanning techniques, FEM provides parallel imaging, i.e., the electrons forming the image are emitted from each atomic site simultaneously.

The experimental approach is illustrated in Fig. 1B: The sample was characterized by SEM (Fig. 1A) and the surface crystallography was deduced from the stereographic projection by combining SEM and FEM images (inset in Fig. 1A, see supplementary text S1 and fig. S1 (22)). The FEM chamber was operated as flow reactor under reactant pressures in the 10^{−5} to 10^{−6} mbar range (Fig. 1B). The local reaction kinetics of individual nanosized Rh(*hkl*) domains of the surface sample were extracted from real-time FEM-video-files following the recently developed approach (23).

Catalytic hydrogen oxidation follows the Langmuir-Hinshelwood mechanism, i.e., the reactants hydrogen and oxygen both first dissociatively adsorb on the catalyst surface, before they react to water, which desorbs immediately at the given reaction temperatures (24). Under specific conditions (both in vacuum and atmospheric pressure, temperatures above 300 K), the H₂ oxidation reaction rate on platinum and rhodium may oscillate between its catalytically active and inactive states in a self-sustained way despite of constant external parameters such as temperature and pressure of reactants (25–27). Different feedback mechanisms governing the oscillations in surface reactions, such as surface reconstruction, subsurface oxygen and oxide formation, were discussed in the literature (25–29). In the present case, fine tuning of experimental conditions plays a crucial role, allowing subsurface oxygen formation, but preventing oxidation of the specimen surface, as will be shown below. Apart from fundamental science, oscillating modes of catalytic reactions may also have

technological impact: periodic operation regimes can improve catalytic reactor performance (30) or enable tuning of surface activity (31).

We studied the oscillating mode of H₂ oxidation on the faceted Rh particle at constant partial pressures of p_{O₂} = 4.4 × 10^{−6} mbar, p_{H₂} = 4.8 × 10^{−6} mbar and different constant temperatures of 413 K, 433 K, and 453 K. At 413 K, oscillations occurred in a synchronized way on almost all particle facets, apart from the central non-oscillating Rh(001) facet (Fig. 2A). This is evident from the FEM intensity curves for regions of interest (ROIs) placed on the Rh(135), Rh(111), Rh(115) and Rh(001) nanofacets. The parallel imaging principle of FEM allowed the construction of a frequency map (bottom panel of Fig. 2A) that showed synchronized oscillations on different individual facets. Details on the construction of the frequency map are presented in supplementary text S2 and fig. S2 (22).

Previous nanometer-scale FIM studies of the oscillating hydrogen oxidation on sharp Pt and Rh nanotips revealed that kinetic transitions between the catalytically active and inactive steady states occurred always in a spatially synchronized way over the entire sample surface (26, 32, 33). High vacuum conditions excluded gas-phase reaction coupling so the spatial coupling was provided by surface diffusion of hydrogen (34, 35). Similar global synchronization on the nanometer-scale was observed in CO oxidation and NO reduction, suggesting that these catalytic reactions (and therein occurring self-sustaining oscillations) in nanosystems are spatially synchronized over the entire particle surface (33–38). However, as shown below, this does not hold true under certain conditions.

When the sample temperature was increased from 413 to 433 K, the reaction exhibited local multifrequential oscillations (Fig. 2B), where the peripheral {111} regions (blue in the frequency map of Fig. 2B) oscillated independently from the surrounding extended (yellow) sample region, despite being separated only by tens of nanometers. The independence of oscillations on different facets demonstrates the intraparticle heterogeneity. The frequencies differed up to 3.8-fold, as illustrated by the FEM intensity curves in Fig. 2B (middle panel). The oscillations from the extended area also partially permeated into the central region, so that the non-oscillating area shrank. The nascent oscillating part of the previously non-oscillating central region (green in the frequency map of Fig. 2B) showed a double-period-like feature, presumably resulting from the interaction of perturbing reaction fronts (infiltrating from the surrounding yellow region) and the natural period of {115} regions, which is governed by the local feed-back mechanism involving the formation of subsurface oxygen (27, 39).

At 453 K, the region with the double-period became synchronized with the ring-shaped surrounding (red region in Fig. 2C), which in turn contracted and increased in its

frequency from 2.7 to 4.3 mHz. The peripheric {111} regions continued to oscillate fully independently from the rest of the sample and each other, but with increased frequencies (see supplementary text S3 and fig. S3 (22)).

The observed behavior was surprising, since the surface diffusion length of hydrogen (in the sub-micrometer range) greatly exceeded the distance between any two sample facets and would have synchronized the oscillations on the different nanofacets. Apparently, the spatial coupling collapsed in the present case, even though obstacles that can cause such collapse, such as grain boundaries between micrometer-sized domains of a polycrystal (40), were not present on the curved Rh particle. The nanofacets were separated solely by nanoridges and nanometer-sized regions of stepped surfaces.

As demonstrated recently (27, 39), the oscillations in H_2 oxidation on Rh are generated by the periodic formation and depletion of subsurface oxygen, so the observed behavior may be related to local peculiarities of periodic subsurface oxygen formation and depletion and to the coupling of this process with neighboring regions. Under the pressure conditions used, qualitative changes in oscillations occurred between 413 and 433 K, whereas the changes observed between 433 and 453 K were mainly quantitative, so we focused on processes on the Rh surface occurring between 413 and 433 K. In this temperature interval, the (1×2) missing row reconstruction on Rh{011} and Rh{113} facets (41, 42) and step-doubling reconstruction on the (111)-oriented terraces of vicinal Rh surfaces (43) take place. Thus, at the two different temperatures (Fig. 2, A and B), the reaction proceeded on different crystallographic surfaces (see the corresponding ball models in Fig. 2).

These changes in surface crystallography and temperature altered the propagation of reaction fronts and impeded their spreading to certain areas. Because the oscillation frequencies are transported with reaction fronts, the synchronized regions in the frequency map corresponded to the areas of front circulation (see supplementary text S4 and figs. S4 and S5) (22). The protruding atomic rows created by the reconstruction effectively hindered the expansion of oscillating fronts from or toward the {111} regions and decoupled these regions from the central oscillating area. In fact, the protruding atomic rows functioned as nanosized frequency transformers and allowed different nanofacets to support different oscillatory regimes.

The increased local roughness of the particle surface also modified the local kinetics of subsurface oxygen formation and changed the frequency of oscillations (compare Fig. 2, A and B). Note that this reaction does not oscillate on the Rh(111) single crystal surface nor on the (111)-oriented domains of a Rh foil (39). The unexpected oscillations of the Rh{111} regions can be explained by the regular steps on these regions caused by the hemispherical particle shape (as

marked in Fig. 1), whereas sporadic steps on the planar Rh{111} surfaces cannot generate oscillations. The sufficient density of steps facilitating subsurface oxygen formation was shown to be a requirement for oscillations in H_2 oxidation on Rh surfaces (39). Under the present conditions, subsurface oxide formation does not result in surface oxide formation due to kinetic limitations of surface oxide formation (44). Since the reaction does not oscillate on the oxidized Rh surface, balancing the narrow range between the subsurface oxygen formation and Rh surface oxidation is crucial for the present observations.

To reveal the reactivity and decoupling function of the highly corrugated regions between the {111} facets and the central part of the sample, the catalytically active sites were directly imaged. For the visualization of catalytically active sites, the ionized reaction product water, forming H_3O^+ and a small amount of H_2O^+ ions (45), was used as imaging species in the FIM mode of our microscope. Corresponding water-FIM images obtained in situ during the kinetic transition from the inactive (O covered) to the active state (Fig. 3) at 393 K not only illustrate the transition itself, but also revealed the decoupling function of the highly corrugated regions separating the {111} facets and the central area of the sample. The water production (bright regions) started in the vicinity of {112} facets, which appeared to be the most active, and then spread almost over the entire surface.

The slow-motion frames (Fig. 3B) and a scheme showing the front propagation (numbered front contours in Fig. 3C) demonstrate that the reaction front did not cross the (113) facet (because of the presence of protruding atomic rows) and hence did not proceed toward the central (001) plane. Rather, the front propagated toward the (111) facet (front contours 1 to 5 in Fig. 3C) and was eventually diverted around the (111) facet because of the double-step reconstructions surrounding the (111) vicinals (front contours 6 to 9 in Fig. 3C).

To deepen the understanding of the observed effects, we performed microkinetic simulations on a model describing oscillations in H_2 oxidation on Rh caused by field-enhanced surface oxidation of Rh and observed by FIM (38). In the present FEM studies, such effects that result from the field-induced electron-density redistribution cannot occur since the field strengths were significantly lower, and, much more importantly, because of the opposite direction of the field vector (unlike FIM, the sample is negatively charged in FEM). The electrostatic field of ≤ 4 V/nm applied in the FEM did not influence the catalytic H_2 oxidation (for details see the supplementary text S5 and the discussion in the Ref. 20), so we modified the model for the present quasi field-free case (for details see the supplementary text S6).

In this subsurface oxygen feedback model, two steady states (high activity $\leftrightarrow$ low activity) periodically switch through a coverage-dependent sticking coefficient of oxygen.

The high initial sticking coefficient of oxygen on metallic Rh leads to a high coverage of adsorbed oxygen O_{ads} (inactive state) and subsequent formation of subsurface oxygen O_{sub} (39). The presence of O_{sub} reduces the sticking of oxygen on the surface, and hydrogen competitively coadsorbs with oxygen and reduces the coverage of O_{ads} and O_{sub} to their initial values to start the next cycle (for details of the cycle and of the model calculations see supplementary text S6 and fig. S6) (22). Figure 4A shows the calculated oscillations in oxygen coverage on the Rh surface for the present conditions. Such oscillations of the oxygen coverage caused oscillating variations of the surface work function which are captured in the experiments as variations of the FEM image intensity. To represent different facets, Fig. 4B shows the temperature dependence of the oscillation frequency for three different activation energies of subsurface oxygen formation E_{ox} in comparison with the experimental data from Fig. 2.

Solitary atomic size surface features were shown to govern the catalytic behavior of an entire sub-micrometer particle via interfacet communication. Choosing a surface containing “pacemaker nanofacets” large enough to undergo surface reconstruction, but still with a curvature radius that enabled FEM imaging, was crucial for revealing the new effects. The interfacet communication ensured that oscillations remained single frequency within the unicolor areas in the frequency maps (compare the yellow, blue and green regions in Fig. 2B), although differently oriented nanofacets within these areas should in principle exhibit different frequencies (as the different domains of a polycrystal indeed do) (27, 39). The “natural” frequencies would be governed by the rate of subsurface oxygen formation and depletion, which is structure dependent (39). In the present case, many differently oriented facets of the Rh particle oscillate with a “forced” rather than their “natural” frequency. The heterogeneous surface thus behaves as an extended system of diffusively coupled oscillators, exhibiting effects such as entrainment and frequency-locking which are characteristic for these systems (46, 47).

REFERENCES AND NOTES

1. P. Nolte, A. Stierle, N. Y. Jin-Phillipp, N. Kasper, T. U. Schulli, H. Dosch, Shape changes of supported Rh nanoparticles during oxidation and reduction cycles. *Science* **321**, 1654–1658 (2008). [doi:10.1126/science.1160845](https://doi.org/10.1126/science.1160845) [Medline](#)
2. M. E. Grass, Y. Zhang, D. R. Butcher, J. Y. Park, Y. Li, H. Bluhm, K. M. Bratlie, T. Zhang, G. A. Somorjai, A reactive oxide overlayer on rhodium nanoparticles during CO oxidation and its size dependence studied by in situ ambient-pressure X-ray photoelectron spectroscopy. *Angew. Chem. Int. Ed.* **47**, 8893–8896 (2008). [doi:10.1002/anie.200803574](https://doi.org/10.1002/anie.200803574) [Medline](#)
3. D. Neagu, T.-S. Oh, D. N. Miller, H. Ménard, S. M. Bukhari, S. R. Gamble, R. J. Gorte, J. M. Vohs, J. T. S. Irvine, Nano-socketed nickel particles with enhanced coking resistance grown in situ by redox exsolution. *Nat. Commun.* **6**, 8120 (2015). [doi:10.1038/ncomms9120](https://doi.org/10.1038/ncomms9120) [Medline](#)
4. T. W. Hansen, A. T. Delariva, S. R. Challa, A. K. Datye, Sintering of catalytic nanoparticles: Particle migration or Ostwald ripening? *Acc. Chem. Res.* **46**, 1720–1730 (2013). [doi:10.1021/ar3002427](https://doi.org/10.1021/ar3002427) [Medline](#)
5. T. W. Hansen, J. B. Wagner, P. L. Hansen, S. Dahl, H. Topsøe, C. J. H. Jacobsen, Atomic-resolution in situ transmission electron microscopy of a promoter of a heterogeneous catalyst. *Science* **294**, 1508–1510 (2001). [doi:10.1126/science.1064399](https://doi.org/10.1126/science.1064399) [Medline](#)
6. M. Plodinec, H. C. Nerl, F. Girgsdies, R. Schlögl, T. Lunkenbein, Insights into chemical dynamics and their impact on the reactivity of Pt nanoparticles during CO oxidation by operando TEM. *ACS Catal.* **10**, 3183–3193 (2020). [doi:10.1021/acscatal.9b03692](https://doi.org/10.1021/acscatal.9b03692)
7. R. Reske, H. Mistry, F. Beharfarid, B. Roldan Cuenya, P. Strasser, Particle size effects in the catalytic electroreduction of CO_2 on Cu nanoparticles. *J. Am. Chem. Soc.* **136**, 6978–6986 (2014). [doi:10.1021/ja500328k](https://doi.org/10.1021/ja500328k) [Medline](#)
8. Y. Li, X.-P. Wu, N. Jiang, M. Lin, L. Shen, H. Sun, Y. Wang, M. Wang, X. Ke, Z. Yu, F. Gao, L. Dong, X. Guo, W. Hou, W. Ding, X.-Q. Gong, C. P. Grey, L. Peng, Distinguishing faceted oxide nanocrystals with ^{17}O solid-state NMR spectroscopy. *Nat. Commun.* **8**, 581 (2017). [doi:10.1038/s41467-017-00603-7](https://doi.org/10.1038/s41467-017-00603-7) [Medline](#)
9. S. Dery, E. Amit, E. Gross, Identifying catalytic reactions on single nanoparticles. *Top. Catal.* **61**, 923–939 (2018). [doi:10.1007/s11244-018-0931-4](https://doi.org/10.1007/s11244-018-0931-4)
10. A. Lassenberger, T. A. Grünewald, P. D. J. van Oostrum, H. Rennohofer, H. Amenitsch, R. Zirbs, H. C. Lichtenegger, E. Reimhult, Monodisperse iron oxide nanoparticles by thermal decomposition: Elucidating particle formation by second-resolved in situ small-angle X-ray scattering. *Chem. Mater.* **29**, 4511–4522 (2017). [doi:10.1021/acs.chemmater.7b01207](https://doi.org/10.1021/acs.chemmater.7b01207) [Medline](#)
11. Y. Liu, F. Meirer, C. M. Krest, S. Webb, B. M. Weckhuysen, Relating structure and composition with accessibility of a single catalyst particle using correlative 3-dimensional micro-spectroscopy. *Nat. Commun.* **7**, 12634 (2016). [doi:10.1038/ncomms12634](https://doi.org/10.1038/ncomms12634) [Medline](#)
12. Y. Ebenstein, T. Mokari, U. Banin, Fluorescence quantum yield of CdSe/ZnS nanocrystals investigated by correlated atomic-force and single-particle fluorescence microscopy. *Appl. Phys. Lett.* **80**, 4033–4035 (2002). [doi:10.1063/1.1482785](https://doi.org/10.1063/1.1482785)
13. P. Tabib Zadeh Adibi, T. Pingel, E. Olsson, H. Grönbeck, C. Langhammer, Plasmonic nanospectroscopy of platinum catalyst nanoparticle sintering in a mesoporous alumina support. *ACS Nano* **10**, 5063–5069 (2016). [doi:10.1021/acsnano.5b07861](https://doi.org/10.1021/acsnano.5b07861) [Medline](#)
14. Y. Suchorski, S. M. Kozlov, I. Bespalov, M. Datler, D. Vogel, Z. Budinska, K. M. Neyman, G. Rupprechter, The role of metal/oxide interfaces for long-range metal particle activation during CO oxidation. *Nat. Mater.* **17**, 519–522 (2018). [doi:10.1038/s41563-018-0080-y](https://doi.org/10.1038/s41563-018-0080-y) [Medline](#)
15. R. Gomer, Diffusion of adsorbates on metal surfaces. *Rep. Prog. Phys.* **53**, 917–1002 (1990). [doi:10.1088/0034-4885/53/7/002](https://doi.org/10.1088/0034-4885/53/7/002)
16. J. Beben, Y. Suchorski, Surface diffusion by adsorbate density fluctuation measurements. *Prog. Surf. Sci.* **74**, 3–24 (2003). [doi:10.1016/j.progsurf.2003.08.002](https://doi.org/10.1016/j.progsurf.2003.08.002)
17. V. V. Gorodetskii, V. I. Elokhin, J. W. Bakker, B. E. Nieuwenhuys, Field electron and field ion microscopy studies of chemical wave propagation in oscillatory reactions on platinum group metals. *Catal. Today* **105**, 183–205 (2005). [doi:10.1016/j.cattod.2005.03.082](https://doi.org/10.1016/j.cattod.2005.03.082)
18. Y. Suchorski, W. Drachsel, Catalytic reactions on platinum nanofacets: Bridging the size and complexity gap. *Top. Catal.* **46**, 201–215 (2007) and references therein. [doi:10.1007/s11244-007-0330-8](https://doi.org/10.1007/s11244-007-0330-8)
19. C. Barroo, T. V. de Bocarmé, Y. De Decker, N. Kruse, “Surface reactions investigated at the nanoscale by field emission techniques: nonlinear dynamics of the catalytic hydrogenation of NO and NO₂ over platinum crystallites” in *Model studies in heterogeneous catalysis*, K. Wandelt, Ed. (Elsevier, 2018, ed. 1) vol. 2.1 of *Encyclopedia of Interfacial Chemistry*, chap. 25, 251–260.
20. M. Datler, I. Bespalov, S. Buhr, J. Zeininger, M. Stöger-Pollach, J. Bernardi, G. Rupprechter, Y. Suchorski, Hydrogen oxidation on stepped Rh surfaces: μm -scale versus nanoscale. *Catal. Lett.* **146**, 1867–1874 (2016). [doi:10.1007/s10562-016-1824-4](https://doi.org/10.1007/s10562-016-1824-4) [Medline](#)
21. T. Visart de Bocarmé, G. Beketov, N. Kruse, Water formation from O_2 and H_2 on Rh tips: Studies by field ion microscopy and pulsed field desorption mass spectrometry. *Surf. Interface Anal.* **36**, 522–527 (2004). [doi:10.1002/sia.1698](https://doi.org/10.1002/sia.1698)
22. Materials and methods are available as supplementary materials.
23. Y. Suchorski, G. Rupprechter, Local reaction kinetics by imaging. *Surf. Sci.* **643**, 52–58 (2016). [doi:10.1016/j.susc.2015.05.021](https://doi.org/10.1016/j.susc.2015.05.021) [Medline](#)

24. L. K. Verheij, M. B. Hugenschmidt, On the mechanism of the hydrogen–oxygen reaction on Pt(111). *Surf. Sci.* **416**, 37–58 (1998). [doi:10.1016/S0039-6028\(98\)00498-1](https://doi.org/10.1016/S0039-6028(98)00498-1)
25. R. Imbihl, G. Ertl, Oscillatory kinetics in heterogeneous catalysis. *Chem. Rev.* **95**, 697–733 (1995). [doi:10.1021/cr00035a012](https://doi.org/10.1021/cr00035a012)
26. J.-S. McEwen, P. Gaspard, T. V. de Bocarmé, N. Kruse, Nanometric chemical clocks. *Proc. Natl. Acad. Sci. U.S.A.* **106**, 3006–3010 (2009). [doi:10.1073/pnas.0811941106](https://doi.org/10.1073/pnas.0811941106) [Medline](#)
27. Y. Suchorski, M. Datler, I. Bepalov, J. Zeininger, M. Stöger-Pollach, J. Bernardi, H. Grönbeck, G. Rupprechter, Visualizing catalyst heterogeneity by a multifrequency oscillating reaction. *Nat. Commun.* **9**, 600 (2018). [doi:10.1038/s41467-018-03007-3](https://doi.org/10.1038/s41467-018-03007-3) [Medline](#)
28. Y. Suchorski, W. Drachsel, V. Gorodetskii, V. Medvedev, H. Weiss, Lifted reconstruction as a feedback mechanism in the oscillating CO oxidation on Pt nanofacets: Microscopic evidences. *Surf. Sci.* **600**, 1579–1585 (2006). [doi:10.1016/j.susc.2005.11.060](https://doi.org/10.1016/j.susc.2005.11.060)
29. G. Ertl, Reactions at surfaces: From atoms to complexity (Nobel Lecture). *Angew. Chem. Int. Ed.* **47**, 3524–3535 (2008). [doi:10.1002/anie.200800480](https://doi.org/10.1002/anie.200800480) [Medline](#)
30. F. J. M. Horn, R. C. Lin, Periodic processes: A variational approach. *Ind. Eng. Chem. Process Des. Dev.* **6**, 21–30 (1967). [doi:10.1021/i260021a005](https://doi.org/10.1021/i260021a005)
31. J. Wolff, A. G. Papathanasiou, I. G. Kevrekidis, H. H. Rotermund, G. Ertl, Spatiotemporal addressing of surface activity. *Science* **294**, 134–137 (2001). [doi:10.1126/science.1063597](https://doi.org/10.1126/science.1063597) [Medline](#)
32. V. Gorodetskii, J. H. Block, W. Drachsel, Isothermal oscillations of the hydrogen-oxidation reaction on platinum: Investigations in the field electron and field ion microscope. *Appl. Surf. Sci.* **76–77**, 129–135 (1994). [doi:10.1016/0169-4332\(94\)90333-6](https://doi.org/10.1016/0169-4332(94)90333-6)
33. T. Visart de Bocarmé, T.-D. Chau, N. Kruse, Imaging and probing catalytic surface reactions on the nanoscale: Field ion microscopy and atom-probe studies of O₂-H₂/Rh and NO-H₂/Pt. *Top. Catal.* **39**, 111–120 (2006). [doi:10.1007/s11244-006-0044-3](https://doi.org/10.1007/s11244-006-0044-3)
34. C. Barroo, Y. De Decker, T. Visart de Bocarmé, N. Kruse, Emergence of chemical oscillations from nanosized target patterns. *Phys. Rev. Lett.* **117**, 144501 (2016). [doi:10.1103/PhysRevLett.117.144501](https://doi.org/10.1103/PhysRevLett.117.144501) [Medline](#)
35. V. Gorodetskii, J. Lauterbach, H. H. Rotermund, J. H. Block, G. Ertl, Coupling between adjacent crystal planes in heterogeneous catalysis by propagating reaction–diffusion waves. *Nature* **370**, 276–279 (1994). [doi:10.1038/370276a0](https://doi.org/10.1038/370276a0)
36. V. Medvedev, Y. Suchorski, Li-modified oscillations in CO oxidation on a Pt field emitter tip. *Surf. Sci.* **364**, L540–L546 (1996). [doi:10.1016/0039-6028\(96\)00729-7](https://doi.org/10.1016/0039-6028(96)00729-7)
37. T. Visart de Bocarmé, G. Beketov, N. Kruse, Water formation from O₂ and H₂ on Rh tips: Studies by field ion microscopy and pulsed field desorption mass spectrometry. *Surf. Interface Anal.* **36**, 522–527 (2004). [doi:10.1002/sia.1698](https://doi.org/10.1002/sia.1698)
38. J.-S. McEwen, P. Gaspard, T. Visart de Bocarmé, N. Kruse, Oscillations and bistability in the catalytic formation of water on rhodium in high electric fields. *J. Phys. Chem.* **113**, 17045–17058 (2009).
39. Y. Suchorski, M. Datler, I. Bepalov, J. Zeininger, M. Stöger-Pollach, J. Bernardi, H. Grönbeck, G. Rupprechter, Surface-structure libraries: Multifrequency oscillations in catalytic hydrogen oxidation on rhodium. *J. Phys. Chem. C Nanomater. Interfaces* **123**, 4217–4227 (2019). [doi:10.1021/acs.jpcc.8b11421](https://doi.org/10.1021/acs.jpcc.8b11421) [Medline](#)
40. C. Spiel, D. Vogel, R. Schlögl, G. Rupprechter, Y. Suchorski, Spatially coupled catalytic ignition of CO oxidation on Pt: Mesoscopic versus nano-scale. *Ultramicroscopy* **159**, 178–183 (2015). [doi:10.1016/j.ultramic.2015.05.012](https://doi.org/10.1016/j.ultramic.2015.05.012) [Medline](#)
41. P. W. Murray, F. M. Leibsle, Y. Li, Q. Guo, M. Bowker, G. Thornton, V. R. Dhanak, K. C. Prince, R. Rosei, Scanning-tunneling-microscopy study of the oxygen-induced reconstruction of Rh(110). *Phys. Rev. B Condens. Matter* **47**, 12976–12979 (1993). [doi:10.1103/PhysRevB.47.12976](https://doi.org/10.1103/PhysRevB.47.12976) [Medline](#)
42. C. Voss, A. Gaussmann, N. Kruse, Oxygen-induced reconstruction of Rh{110} and {113} single crystal planes. *Appl. Surf. Sci.* **67**, 142–146 (1993). [doi:10.1016/0169-4332\(93\)90306-V](https://doi.org/10.1016/0169-4332(93)90306-V)
43. G. Hoogers, D. A. King, Adsorbate-induced step-doubling reconstruction of a vicinal metal surface: Oxygen on Rh {332}. *Surf. Sci.* **286**, 306–316 (1993). [doi:10.1016/0039-6028\(93\)90414-F](https://doi.org/10.1016/0039-6028(93)90414-F)
44. P. Winkler, J. Zeininger, Y. Suchorski, M. Stöger-Pollach, P. Zeller, M. Amati, L. Gregoratti, G. Rupprechter, How the anisotropy of surface oxide formation influences the transient activity of a surface reaction. *Nat. Commun.* **12**, 69 (2021). [doi:10.1038/s41467-020-20377-9](https://doi.org/10.1038/s41467-020-20377-9) [Medline](#)
45. N. Ernst, G. Bozdech, V. Gorodetskii, J. H. Block, Field ion spectroscopy of oscillating surface reactions: H₂/O₂ and H₂/H₂O on platinum. *Int. J. Mass Spectrom.* **152**, 185–191 (1996). [doi:10.1016/0168-1176\(95\)04332-2](https://doi.org/10.1016/0168-1176(95)04332-2)
46. D. Krefting, P. Kaira, H. H. Rotermund, Period doubling and spatiotemporal chaos in periodically forced CO oxidation on Pt(110). *Phys. Rev. Lett.* **102**, 178301 (2009). [doi:10.1103/PhysRevLett.102.178301](https://doi.org/10.1103/PhysRevLett.102.178301) [Medline](#)
47. P. S. Bodega, P. Kaira, C. Beta, D. Krefting, D. Bauer, B. Mirwald-Schulz, C. Punckt, H. H. Rotermund, High frequency periodic forcing of the oscillatory catalytic CO oxidation on Pt(110). *New J. Phys.* **9**, 61 (2007). [doi:10.1088/1367-2630/9/3/061](https://doi.org/10.1088/1367-2630/9/3/061)
48. Y. Suchorski, J. Zeininger, S. Buhr, M. Raab, M. Stöger-Pollach, J. Bernardi, H. Grönbeck, G. Rupprechter, Resolving multifrequency oscillations and nanoscale interfacet communication in single particle catalysis - Database S1. Zenodo (2021); [doi:10.5281/zenodo.4709843](https://doi.org/10.5281/zenodo.4709843)
49. V. V. Gorodetskii, B. E. Nieuwenhuys, Chemisorption and dissociation of carbon monoxide on rhodium surfaces. *Surf. Sci.* **105**, 299–312 (1981). [doi:10.1016/0039-6028\(81\)90163-1](https://doi.org/10.1016/0039-6028(81)90163-1)
50. V. K. Medvedev, Y. Suchorski, C. Voss, T. Visart de Bocarmé, T. Bär, N. Kruse, Oxygen-induced reconstruction and surface oxidation of rhodium. *Langmuir* **14**, 6151–6157 (1998). [doi:10.1021/la980603c](https://doi.org/10.1021/la980603c)
51. F. Mertens, R. Imbihl, A. Mikhailov, Breakdown of global coupling in oscillatory chemical reactions. *J. Chem. Phys.* **99**, 8668–8671 (1993). [doi:10.1063/1.465590](https://doi.org/10.1063/1.465590)
52. R. H. Good, E. W. Müller, “Field emission” in *Electron emission. Gas discharges.*, S. Flügge, Ed. (Springer, 1956, ed. 1) vol 4 of *Encyclopedia of Physics / Handbuch der Physik*, chap. 2, 176–231.
53. Y. Suchorski, W. A. Schmidt, N. Ernst, J. H. Block, H. J. Kreuzer, Electrostatic fields above individual atoms. *Prog. Surf. Sci.* **48**, 121–134 (1995). [doi:10.1016/0079-6816\(95\)93420-C](https://doi.org/10.1016/0079-6816(95)93420-C)
54. Y. Suchorski, Probing adsorption on a nanoscale: Field desorption microspectroscopy. *Adsorption* **23**, 217–224 (2017). [doi:10.1007/s10450-016-9824-7](https://doi.org/10.1007/s10450-016-9824-7) [Medline](#)
55. Y. Suchorski, R. Imbihl, V. K. Medvedev, Compatibility of field emitter studies of oscillating surface reactions with single crystal measurements: Catalytic CO oxidation on Pt. *Surf. Sci.* **401**, 392–399 (1998). [doi:10.1016/S0039-6028\(98\)00043-0](https://doi.org/10.1016/S0039-6028(98)00043-0)
56. J.-S. McEwen, P. Gaspard, T. Visart de Bocarmé, N. Kruse, Electric field induced oscillations in the catalytic water production on rhodium: A theoretical analysis. *Surf. Sci.* **604**, 1353–1368 (2010). [doi:10.1016/j.susc.2010.04.007](https://doi.org/10.1016/j.susc.2010.04.007)
57. M. P. Zum Mallen, W. R. Williams, L. D. Schmidt, Steps in hydrogen oxidation on rhodium: Hydroxyl desorption at high temperatures. *J. Phys. Chem.* **97**, 625–632 (1993) and references therein. [doi:10.1021/ji00105a016](https://doi.org/10.1021/ji00105a016)
58. G. Ertl, Oscillatory catalytic reactions at single-crystal surfaces. *Adv. Catal.* **37**, 213–277 (1990). [doi:10.1016/S0360-0564\(08\)60366-1](https://doi.org/10.1016/S0360-0564(08)60366-1)
59. L. Gregoratti, A. Baraldi, V. R. Dhanak, G. Comelli, M. Kiskinova, R. Rosei, Structural effects on water formation from coadsorbed H+O on Rh(100). *Surf. Sci.* **340**, 205–214 (1995). [doi:10.1016/0039-6028\(95\)00695-8](https://doi.org/10.1016/0039-6028(95)00695-8)
60. J.-S. McEwen, P. Gaspard, F. Mittendorfer, T. Visart de Bocarmé, N. Kruse, Field-assisted oxidation of rhodium. *Chem. Phys. Lett.* **452**, 133–138 (2008). [doi:10.1016/j.cplett.2007.12.031](https://doi.org/10.1016/j.cplett.2007.12.031)
61. J. Kiklovits, M. Schmid, L. R. Merte, P. Varga, R. Westerström, A. Resta, J. N. Andersen, J. Gustafson, A. Mikkelsen, E. Lundgren, F. Mittendorfer, G. Kresse, Step-orientation-dependent oxidation: From 1D to 2D oxides. *Phys. Rev. Lett.* **101**, 266104 (2008). [doi:10.1103/PhysRevLett.101.266104](https://doi.org/10.1103/PhysRevLett.101.266104) [Medline](#)

ACKNOWLEDGMENTS

Funding: This work was supported by the Austrian Science Fund (FWF) (P 32772-N and SFB F45 FOXS) and by the Swedish Research Council (2020-05191).
Author contributions: J.Z. and S.B. performed the FEM/FIM experiments, J.Z. and M.R. carried out processing of the FEM/FIM video-files, M.S.-P. and J.B. made the SEM characterization of the sample. H.G. performed the microkinetic modelling. Y.S. and G.R. supervised the experimental work and were involved in the analysis of the experimental data. Y.S., G.R. and H.G. prepared the

manuscript. All authors contributed to the discussion and approved the manuscript and supporting information. **Competing interests:** The authors declare no competing interests. **Data and materials availability:** The FEM and FIM video data (database S1) that support the findings of this study are available as zipped HDF5 files in a Zenodo repository under <https://doi.org/10.5281/zenodo.4709843> (48). The data used for modelling is detailed in supplementary text S6 and table S1.

SUPPLEMENTARY MATERIALS

science.sciencemag.org/cgi/content/full/science.abf8107/DC1

Materials and Methods

Supplementary Text

Figs. S1 to S6

Table S1

References (49–61)

Movies S1 to S3

20 November 2020; resubmitted 17 February 2021

Accepted 5 May 2021

Published online 20 May 2021

10.1126/science.abf8107

Fig. 1. Apex of a curved Rh crystal as a single catalytic particle. (A) SEM micrograph of the Rh specimen with a crystallographic net as overlayer (radius of the hemispherical apex 650 nm). The inset shows the corresponding FEM micrograph with nanofacets indicated. (B) schematics of the experiment: electrons, field-emitted from the sample surface, create a projection image on the screen. The FEM chamber is used as flow reactor and the FEM image brightness reflects the local reaction rate. The locally magnified schematic shows a Rh(111) nanofacet with a reaction front between the catalytically active and inactive surface.

Fig. 2. Oscillations in the catalytic H_2 oxidation reaction. Imaging of the curved Rh crystal shown in Fig. 1A, observed by FEM at $p_{\text{O}_2} = 4.4 \times 10^{-6}$ mbar, $p_{\text{H}_2} = 4.8 \times 10^{-6}$ mbar and at constant temperatures (413, 433, and 453 K). Left side: FEM intensity curves. Right side top panels: FEM video-frames (1.1 μm by 1.1 μm each). Right side bottom panels: frequency maps and crystallography. (A) $T = 413$ K; Regions of interest (ROIs) (40 nm by 40 nm) for the FEM intensity curves are placed in the (135), (111), (115) and (001) regions (compare with Fig. 1). (B) $T = 433$ K; all ROIs are the same as in (A); (C) $T = 453$ K, ROIs correspond to those in (A) and (B). The insets in the bottom right panels show unreconstructed (A) and reconstructed (B) stepped (113) and (111) facets as well as in (C) arrangements of Rh(hkl) facets within a segment marked by the white dotted line, with positions of ROIs marked by red squares.

Fig. 3. FIM mapping of active sites on the curved Rh crystal during hydrogen oxidation using ionized product (water) species as imaging ions. (A) FIM images taken during the kinetic transition from the inactive to the active state (frame size 1.1 μm by 1.1 μm). The evolution of water production over the whole Rh curved crystal surface is shown. (B) "Slow motion" snapshots of the magnified yellow square region (580 nm by 580 nm) marked in (A) taken at 0, 1.8 and 2.2 s; (C) left: crystallographic map according to the FIM images in (A); right: magnified region from (B) with contours of the reaction front, demonstrating the predominant directions of the reaction front propagation. The numbered front contours 1-9 correspond to 1.8, 1.9, 2.0, 2.1, 2.2, 2.4, 2.7, 3.0, and 3.6 s, respectively.

Fig. 4. Simulations of the kinetic oscillations at O₂ and H₂ pressures of 4.4×10^{-6} mbar and 4.8×10^{-6} mbar, respectively. (A) Coverage of oxygen as a function of time with activation energy of subsurface oxygen formation $E_{\text{ox}} = 1.100$ eV at 415 K (upper panel) and 440 K (lower panel). (B) Frequency of the oscillations as a function of temperature for $E_{\text{ox}} = 1.085$ eV (circles), $E_{\text{ox}} = 1.100$ eV (squares) and $E_{\text{ox}} = 1.108$ eV (triangles). Red symbols: experimental frequency data obtained at the {135} nanofacets from Fig. 2.