Transmitting metal–oxide interaction by solitary chemical waves: H₂ oxidation on ZrO₂ supported Rh

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1. Introduction

Despite decades of intense discussions, interactions between metal nanoparticles and the oxidic substrate in supported catalysts remain a hot topic in catalysis [1–4]. Particularly, the atomic details of the diversity of such interactions and their role in reaction mechanisms are still not fully understood. This is, inter alia, due to difficulties in elucidating the structural, size and bonding effects, which can hardly be separated from each other [5]. A particular role in the support-contribution to the reaction kinetics is played by metal-support boundary effects. These borderline sites (also called “adlineation” sites [6,7,8]) along the metal–oxide interface have modified adsorption properties different from the pure metal sites. Until recently, such interactions were believed to be localized, affecting only the reactivity of sites that are near (<1 nm) the interface. However, our recent studies of catalytic CO oxidation on oxide supported palladium particles demonstrated that such interactions may also cause long-ranging effects [9]. Indeed, the atomically narrow metal–oxide interface of Pd aggregates supported by Al₂O₃ or ZrO₂ influenced the metal active sites even thousands nm away from the metal–oxide interface. As a consequence, also the global kinetics of macroscopic samples containing hundreds of Pd aggregates is influenced, making the whole system significantly more resistant to CO poisoning.

In this contribution, we extend this concept to the catalytic hydrogen oxidation on rhodium. As a model system, µm-sized Rh powder agglomerates supported by thin ZrO₂ film were used. Due to the large size, pronounced size effects and electronic structure modifications, as typical for nm-sized metal particles [10,11], should not occur. The chosen µm-scale also enabled the in situ PEEM monitoring of the local reaction front propagation over the surface of individual Rh agglomerates. A rather non-reducible oxide (ZrO₂) was used instead of reducible metal oxides, as e.g. FeOₓ, TiO₂ or CeO₂, to avoid complications by additional oxygen supply from the oxide to the reaction zone. The evaluation was made by the local kinetics by imaging approach recently developed to study the reaction on individual µm-sized domains of polycrystalline Pt and Pd foils (Fig. 1a) [12]. The current results, obtained for the Rh/ZrO₂ model system, reveal a long-ranging support effect in the H₂ oxidation reaction, that is absent for unsupported Rh. This specific effect, originating from a tiny (<1 nm) interface along the perimeter of each individual Rh agglomerate is transmitted over the entire agglomerate, i.e. via thousands of nm by propagating solitary chemical waves.

2. Experimental

To study H₂ oxidation on Rh in situ, an all-metal UHV setup consisting of separate PEEM and XPS chambers, connected with each other by a sample transfer line, was used as a flow reactor. The reactants (O₂ and H₂ gases) were dosed by precision leak valves and the reaction product H₂O was continuously pumped off by a turbomolecular pump.
The ongoing reaction was visualized in real time by PEEM (STAIB) and the images were recorded by a high-speed CCD camera (Hamamatsu). The PEEM magnification, which allows visualization of the reaction on individual µm-sized Rh agglomerates, was calibrated by comparison of PEEM images with optical micrographs of the same sample. The sample consisted of oxidized polycrystalline Zr foil (10 × 10 mm, thickness 0.2 mm, MaTeck, 99.8%) and Rh aggregates (Alfa Aesar 99.9%, 50–100 µm size, thickness few µm) mechanically pressed onto the foil (Fig. 1b). Details of Zr foil oxidation and XPS evaluation of oxide composition and oxide layer thickness were described in detail in Ref. [13]. After repeated standard UHV cleaning procedures (Ar⁺ sputtering and annealing), the cleanliness of the sample was confirmed by XPS before each single reaction measurement. The sample temperature was measured by a Ni/NiCr thermocouple spot-welded directly to the sample.

### 3. Local kinetics by imaging

A straightforward correlation between the coverage-dependent work function of a Pt surface covered by reactants and its catalytic activity was experimentally established for catalytic CO oxidation in the early 1990s [14]. Hence, the “work function governed” image intensity in electron emission microscopes, such as PEEM (photoemission electron microscope), may provide information on the catalytic activity of the imaged surface, at least for reactions such as CO oxidation. This approach was often used, but mainly for qualitative PEEM observations of CO oxidation on uniform single crystal surfaces of Pt-group metals, in which the quantitative information about the reaction kinetics was derived from mass spectrometric (MS) measurements, performed simultaneously with PEEM observations [15–17]. However, for spatially heterogeneous surfaces of model catalysts, the MS approach reaches its limit, due to its area-averaging principle: MS cannot distinguish between product species originating from different regions of the sample and can thus not provide the local kinetic data. The use of the “scanning” MS [18] can only partially solve this problem.

This limitation can be lifted, however. Since the correlation of the catalytic activity with the work function (and thus with the image intensity of any work function based microscope) can be scaled down to the resolution limit of the microscope, the local kinetics for small surface areas can be obtained by analysis of the local image intensity. This allows spatially- and component-resolved kinetic studies and, e.g., a direct comparison of inherent catalytic properties of Pt(hkl)- and Pd (hkl)-domains [19,20], or of individual supported µm-sized Pd powder agglomerates [9,21]. The principle underlying this approach is illustrated in Fig. 1a, the basics, experimental details and results for CO oxidation are summarized in a recent review [12].

For H₂ oxidation on Rh, the straightforward correlation between the PEEM image intensity and the H₂O production rate was quantitatively proven by Schaak and Imbihl for a Rh(111) single crystal surface by comparing the MS signal with the PEEM intensity integrated over the whole field of view [22]. Our recent studies of H₂ oxidation on individual µm-sized domains of polycrystalline Rh foil, representing a kind of surface structure library [23], confirmed the validity of such a correlation for H₂ oxidation on the local µm-scale [24].

In this contribution, the same approach was applied for quantitative analysis of kinetic transitions (active → inactive steady state, and vice versa) in H₂ oxidation on µm-sized Rh aggregates supported by thin film ZrO₂. The relatively wide PEEM field of view (~500 µm) allowed studying the reaction kinetics for few individual differently sized Rh aggregates simultaneously (particle size library [23]). Note that the particle morphology or 3D shape may cause small variations of the image contrast [25], but these do not affect the detection of kinetic transitions that are due to variation of external parameters.
4. Results and discussion

4.1. Metal/oxide interface effect

Hydrogen oxidation on platinum group metal surfaces, such as Rh, is a prototypical Langmuir–Hinshelwood reaction in heterogeneous catalysis with the H$_2$O formation rate being mainly determined by the competition between dissociative adsorption of hydrogen and oxygen [22,26,27]. At low H$_2$:O$_2$ gas-flow ratio, the Rh surface is saturated by atomic oxygen, which inhibits the dissociative adsorption of hydrogen (oxygen poisoning [28,29]). As a consequence, the system remains in an inactive steady state. With rising H$_2$:O$_2$ ratio (e.g. by increasing H$_2$ pressure) the spontaneous formation of microscopically small surface regions with adsorbed H atoms can be observed, where OH islands are formed before H$_2$O is produced [28,29]. The spatial extension of this area proceeds as a front, with the hydrogen dissociation blocked ahead of it and occurring in the areas behind (the surface density of adsorbed oxygen in the OH covered areas is higher, creating free sites for dissociative hydrogen adsorption [29]). Due to the high reaction rate, the catalytically active surface behind the front exhibits a low hydrogen coverage which leaves plenty of free sites for oxygen dissociation. The impinging oxygen reacts off, forming H$_2$O which immediately desorbs at the current reaction temperatures. For corrugated Rh surfaces, such as Rh(110), the adsorption induced reconstruction and resulting surface strain additionally contribute to the surface reactivity complicating, however, the detailed microscopic picture [29].

Due to the unequal adsorption properties of oxygen and hydrogen, the cyclewise variation of control parameters, e.g. the $p_{H_2}$ pressure (at constant $p_{O_2}$ and $T$) leads to a hysteresis-like behavior of the reaction rate [22]. Such behavior is typical for a bistable character of a reaction, i.e. for the existence of two steady states (of high and low catalytic activity) with kinetic transitions between them [30]. The propagating reaction fronts mentioned above are "carriers" of such kinetic transitions and can be observed not only on the atomic scale [28,29], but also mesoscopically, e.g. using PEEM with μm-resolution [22,24]. Under certain conditions the reaction may exhibit a number of additional and unusual features, such as appearance of self-sustaining oscillations, triggered by the formation of subsurface oxygen species [31]. Since it was intended to compare the reaction behavior of supported and unsupported Rh conditions, reactions were chosen at which the formation of subsurface oxygen does not occur, i.e. in the oxygen pressure range of 10$^{-7}$–10$^{-6}$ mbar and in the temperature range 433–493 K [32].

To study the bistable behavior of H$_2$ oxidation on ZrO$_2$ supported Rh particles, the ongoing reaction was visualized by PEEM during cyclewise variation of $p_{H_2}$ between 1 × 10$^{-7}$ and 8 × 10$^{-6}$ mbar at constant $T = 453$ K and constant $p_{O_2} = 7.7 × 10^{-7}$ mbar (Fig. 2). The partial pressures of reactants and the temperature were acquired simultaneously to the video-recording. To our knowledge, these are the first successful in situ PEEM images of ongoing H$_2$ oxidation on a supported model catalyst. The local PEEM intensity within a ROI (region of interest corresponding here to a circular surface area with a radius of 20 μm) placed on an individual Rh agglomerate was read out frame-by-frame and plotted vs. the $p_{H_2}$ resulting in the hysteresis curve in Fig. 2. The hysteresis in Fig. 2 shows a steep jump in the local PEEM intensity, corresponding to the kinetic transition $\tau_A$ from the initially inactive (oxygen saturated surface, high work function, dark image contrast) to the active (reduced surface, low work function, bright contrast). The shape of the curve does not depend on the ROI-size and is thus representative for the observed kinetic transition which occurs at characteristic partial pressure $p_{H_2}$ at constant $p_{O_2}$ and temperature. The kinetic transition proceeds via propagation of the reaction front (frames 2 and 3 in Fig. 2) and is caused by the enhanced adsorption of hydrogen at increasing $p_{H_2}$ and its reaction with oxygen, which depletes the O adlayer.

In turn, decreasing $p_{H_2}$ leads to the reverse transition $\tau_B$ from the active to the inactive steady state, visible as a steep drop in the local PEEM intensity. As already mentioned, the PEEM intensity reflects in a straightforward manner the local reaction rate. Thus, the intensity curve in Fig. 2 may be considered as local H$_2$O rate evolution, measured as relative value (arbitrary units). The PEEM snapshots of the reaction front propagation (frames 1–4 in Fig. 2) illustrate how the transition proceeds spatially. Note that the reaction front always nucleates at the edges of the Rh aggregate, i.e. at the metal–oxide interface (see e.g. frame 2 in Fig. 2).

Apparently, the metal-oxide interface provides the most favorable conditions for the initiation of a kinetic transition. However, the interface along the perimeter line is not homogeneous on atomic scale, thus the initiation starts at a short section of the perimeter line, where the conditions are particularly beneficial (see e.g. frame 2 in Fig. 2).

Fig. 2 also shows the corresponding kinetic phase diagram constructed as a plot of transition points $\tau_A$ and $\tau_B$ measured for different temperatures (433–493 K). This way of illustrating the reaction behavior allows an easy identification of regions of high and low activity, as well as of bistability, and is therefore often used for comparison of different model systems, e.g. in CO oxidation [20,33,34].

The term "kinetic phase diagram" is justified by the analogy to equilibrium thermodynamics (cooperative phenomena play a crucial role in both equilibrium and nonequilibrium phase transitions [35,36]); see also the discussion in Refs. [33,34]. The diagram in Fig. 2 thus differentiates the monostable regions of high and low activity from the region of bistability, the width of which slightly varies with temperature. Fig. 2 characterises the individual Rh agglomerate shown in video-frame 1, but diagrams obtained for other Rh agglomerates of different shape and size are identical within experimental accuracy.

To compare the catalytic behavior of supported Rh in H$_2$ oxidation with that of unsupported Rh, a reference model system is necessary. In our recent CO oxidation study of supported Pd, we used Pd agglomerates deposited on polycrystalline Pt as reference system. Since the CO oxidation proceeds independently on Pd and Pt [20,21], Pt-supported Pd can be treated as "quasi-unsupported" (for details see Ref. [9] and SI.
Fig. 3. The same experiment as in Fig. 2, but for unsupported Rh (Ar+ sputtered polycrystalline Rh foil). The row of video-frames illustrates the isothermal (T = 453 K) kinetic transition $\tau_B$ from the inactive to active steady state upon increasing $P_{H_2}$ at constant oxygen pressure of $7.7 \times 10^{-7}$ mbar. The grain boundaries of individual domains and Miller indices (as determined by EBSD) are marked in frame 4. The corresponding hysteresis curve is shown below, the numbers along the curve refer to the video-frames. The blue region in the kinetic phase diagram confines the bistability region, the area above corresponds to the steady state of high reactivity, the area below to the steady state of low reactivity.

Additionally, comparison with an Ar+ sputtered Pd foil revealed that the unsupported Pd aggregates behave (nearly) identical to a polycrystalline Pd surface, 'saturated' with defects by intensive Ar+ sputtering [9,37]. Accordingly, an intensively Ar+ sputtered (afterwards not annealed) Rh foil was employed as 'unsupported' reference system in the current study. Fig. 3 shows the results of the same experiment as in Fig. 2, but for the Ar+ sputtered Rh foil.

Note that the nucleation of the reaction fronts occurs at defects within individual domains and not at the grain boundaries, in contrary to the fronts on oxide supported Rh aggregates, for which the fronts always nucleate at the particle perimeters, i.e. at the metal/oxide interface. In frame 4 of Fig. 3, the orientation of individual Rh(hkl) domains as obtained by electron backscatter diffraction (EBSD) is indicated; for details see Ref. [24]. However, the heavily sputtered Rh(hkl) surfaces lose their individual behavior in H$_2$ oxidation, similar as Pd(hkl) domains do in CO oxidation [37]; the sputtered surface of the entire Rh foil sample behaves in a "uniform" manner.

Fig. 4 compares the kinetic behavior of oxide supported and unsupported Rh in catalytic H$_2$ oxidation. The curves and diagrams in Fig. 4 and direct comparison of video-sequences of kinetic transitions (such as shown e.g. in Fig. 2 and Fig. 3) reveal the following differences: (i) a shift of the diagram for supported Rh to higher H$_2$ pressures as compared to unsupported Rh, for all temperatures studied, (ii) visually observed differences in the position of nucleation (initiation) of the reaction fronts (metal/oxide interface for supported Rh vs defects within the domains, far from the grain boundaries, for unsupported Rh).

This behavior strongly resembles our recent observations of CO oxidation on Pd particles supported by Al$_2$O$_3$ or ZrO$_2$ [9], as well as our earlier studies on the inverse model system of CeO$_2$ islands on a Pt(111) surface [38,39]. For both types of model systems, the kinetic phase diagrams were shifted towards higher pressures of the "poisoning" reactant CO. The similarity of the effect observed for the two different model systems (oxide supported metal and metal supported oxide) highlights the essential role of the metal/oxide interface. Our initial interpretation of the effect observed for a CeO$_2$/Pt(111) interface involved modifications of the precursor potential as well as the dissociation barrier caused by the electron density jump across the interface [39]. Additionally, in the case of reducible oxides, weakly adsorbed oxygen at the edge sites of the oxide (e.g. FeO) [40] may contribute to an enhanced reaction rate. A similar effect may influence the catalytic behavior of Fe$_3$O$_4$ supported nanosized Pd particles, for which a remarkable particle-size dependence of the binding energy of CO and oxygen on particle size was detected [41].

However, energetically modified adsorption sites may also exist on the metal side of the metal/oxide interface, significantly contributing to the modified catalytic behavior. This suggestion was confirmed by recent DFT calculations of the binding energy of CO and O on metal adsorption sites along the metal/oxide interface of supported metal (Pd$_{119}$) particles, which were large enough to exhibit bulk-like properties [9].

An analogous effect, namely the variation of the binding energy of oxygen and hydrogen in the immediate vicinity of the metal/oxide interface likely causes the present effect in H$_2$ oxidation on Rh. To rationalize our observations of H$_2$ oxidation, recent DFT results for O$_{ad}$/Pd [9] and H$_{ad}$/Pd [42] supported by MgO can be consulted. Clearly, Rh is not Pd, but qualitatively the main results of the DFT calculations should also be valid in the present case: (i) the oxygen bonding on the interface-adjacent sites of a supported metal particle is significantly stronger than on the corresponding sites of an unsupported particle, (ii) the support does not influence the adsorption on metal sites distant from the interface (for details, see SI in Ref. [9]), (iii) the binding energy of hydrogen is influenced to a lower degree than that of oxygen. Additionally, the effects calculated for ZrO$_2$ and MgO supports in Ref. [9] are very similar.

Alltogether this allows for an at least qualitative generalisation of the mentioned DFT results and their validity for H$_2$ oxidation on Rh/ZrO$_2$. The geometrical constraints contributing to the interface effect in case of CO oxidation [9], seem to be less pronounced in the present case, due to the dissociative adsorption of both reactants, hydrogen and oxygen.

Thus, since the energetics governs the kinetics of adsorption, the locally enhanced oxygen binding shifts the local oxygen/hydrogen adsorption equilibrium towards the oxygen direction. To compensate this and to initiate the kinetic transition $\tau_B$ to the catalytically active (reduced) Rh surface, a higher hydrogen pressure is necessary. This is also locally valid for the reverse transition $\tau_A$, due to the increased amount of oxygen bonded at the interface, the $\tau_B$ transition should occur.
already at higher H2 pressure for all studied temperatures. However, Fig. 4 demonstrates that this shift occurs not only for the atomically narrow interface region, but also for the mesoscopic Rh aggregate. The remarkable shift of the whole phase diagram for Rh/ZrO2 (Fig. 4) to H2 pressure higher than that for unsupported Rh, indicates that the entire oxide supported Rh aggregate follows the interface-induced transitions. This raises the question how the locally modified kinetics is transmitted from the interface to metal sites on the Rh aggregate that are “far-away”?

### 4.2. Solitary chemical waves

The concept of chemical waves as propagating structured concentration gradients, which arise from an autocatalytic process coupled with mass transport, can be traced back to the pioneering work of Robert Luther published over 80 years ago [43]. In the simplest case of aperiodic propagation in one direction with a constant velocity and constant waveform, one can call that “solitary chemical waves” [44]. In its early development, the concept was mainly attributed to Belousov–Zhabotinsky waves [45] and to chemical wave activity on surfaces of semipermeable membranes [46], but it is also highly suited for surface reactions, for which the term reaction front is also often used [26]. This concept allowed getting insights into the spatial propagation of kinetic transitions in CO oxidation on single crystals [14–17,25] and on µm-sized domains of polycrystalline foils [19–21]. It also helped to understand the role of defects in CO oxidation [36]. Recently, the propagation of chemical waves in CO oxidation on oxide supported Pd aggregates was monitored by PEEM for the first time [9]. Herein, we show the first analogue PEEM observations for H2 oxidation on Rh particles supported by ZrO2. Fig. 5a shows examples of in situ recorded video-frames and a corresponding evaluation of the activation wave propagation over flat regions of the supported Rh aggregate. For comparison, propagation of the activation wave on Rh(111) domains of Ar+-sputtered polycrystalline Rh foil is shown in Fig. 5b.

The evaluation of the propagation velocity on supported Rh aggregates shows that on average it is very similar to that on the Ar+-sputtered Rh surface: under the present conditions, the front propagates in both cases with an approximately constant velocity of ~0.9 µm/s along A → A’ and B → B’ directions, as indicated in Fig. 5a and b. Since the propagation of the chemical waves is very sensitive to the surface structure, it confirms the adequate choice of the Ar+-sputtered Rh surface as (unsupported) reference for oxide supported Rh. This also means that the peculiarities of the propagation of the activation and deactivation waves cannot be responsible for the modified reaction behavior on oxide supported Rh particles. It seems that depending on the reaction, the metal–oxide interface represents the weakest or strongest point of the whole system. Strengthening or weakening the interface with respect to the adsorption of reactants clearly modifies the entire catalyst.

In an earlier study of H2 oxidation on Pt, a comparison between kinetic transitions on a Pt(100) single crystal surface and a Pt(100) facet (~40 nm size) of a Pt nanopit was performed [47]. It appeared that the (100)-facet of the nanopit was “fed” by chemical waves from adjacent crystal planes and kinetic transitions were forced into a parameter range which was far from that observed for the macroscopic Pt(100) single crystal surface. Thus, concentration waves which enter the microscopic Pt(100) facet from “outside” can modify its reactivity. A similar effect was later observed for CO oxidation on Pt [48].

Until now, such a superimposing of catalytic reactivity was observed only for nm-sized surfaces. The present observations of the surface reactivity of oxide supported Rh particles in H2 oxidation, which is modified by chemical waves propagating from the “outside”, are the first of such kind for µm-sized surfaces. It remains astonishing that a very narrow (~1 nm wide) strip of modified adsorption (“adlineation”) sites may influence (on the nanoscale) huge Rh aggregates.
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References