

Model studies of catalysis with microstructured bimetallic surfaces

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Abstract

Microstructured bimetallic surfaces prepared by optical lithography allow us to study dynamic effects under low pressure conditions with spatially resolving in situ techniques such as photoelectron emission microscopy (PEEM) and scanning photoelectron microscopy (SPEM). Reactions of the automotive catalytic converter on microstructured Pt/Rh surfaces have been investigated. The following effects have been observed: macroscopic size effects in reactivity due to diffusional coupling, front nucleation at Pt/Rh domain boundaries and the formation of stationary concentration patterns due to reversible adsorbate-induced segregation in bimetallic alloyed films. The experiments are complemented by simulations of the reactions for composite media aimed at “microchemical engineering” of catalytic surfaces. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In industrial heterogeneous catalysis, catalysts are typically composites whose constituents have been optimized with respect to a desired yield and selectivity. Even today, however, this optimization is done on a purely empirical basis: screening tests narrow down the optimum mixing ratio of the constituents. The interactions between the different constituents, which lead to synergetic effects, are one of the most difficult subjects in basic research. Structural, electronic and transport/dynamic effects are involved and are conceptually difficult to

separate. Bimetallic catalysts provide a prominent example for the synergetic effects present in such composite catalysts [1,2]. The activity and selectivity optimization obtained there is usually discussed in terms of electronic and geometric effects at the atomic scale. Such interactions, however, are difficult to predict and, moreover, mixing at the atomic level is not easily controllable.

Here, we follow a different concept towards a rational design of catalysts. We construct composite surfaces built up by mesoscopic patches of different metals, which are coupled through surface transport. Such composite surfaces with features in the 1–100 μm range can be readily prepared by microlithographic techniques [3–6]. By varying the geometry and dimension of the structures, one can control the diffusional flow between the differently active metals. Due to

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this transport coupling, nonlinear effects become important. The dynamic behavior of the reactions we study (the catalytic NO reduction with CO or H₂ as reducing agent as well as the O₂ + H₂ reaction) are well known from a large number of mostly single crystal studies conducted under low *p* conditions [7,8]. We investigate these reactions in an ultrahigh vacuum (UHV) chamber for $p < 10^{-4}$ mbar, ensuring strict isothermality.

We present a number of examples showing that significant dynamic effects arise when a fast diffusing species is present. These effects can in principle be exploited to “steer” a catalytic reaction. The microstructured samples also provide examples of how complex bimetallic surfaces behave under reaction conditions. We observe that stationary concentration patterns of the adsorbates evolve which are associated with a compositional change of the metallic Pt/Rh substrate. These stationary patterns represent a striking example for the importance of dynamic effects in catalysis because, in our case, the metal catalyst itself represents a dissipative structure.

2. Experimental methods

For spatially resolved in situ measurements, two methods are applied: first, photoelectron emission microscopy (PEEM), which images the local work function with a resolution of ≈ 1 μm but yields no direct information about the chemical identity of the adsorbed species and the chemical state and the composition of the catalyst surface. The missing chemical information is provided by scanning photoelectron microscopy (SPEM) [9,10]. In SPEM, photons (300–900 eV) from a synchrotron source (ELETTRA) are focused into a 0.15- μm spot on the sample. While the sample is scanned photoelectrons are collected with a hemispherical energy analyzer tuned to the energy of a specific core level. In this way, 2D maps of the elemental distribution are generated.

The microstructured model catalyst are constructed in a negative photoresist process in which we deposit a thin metal layers (Pt, Rh, Ti; thickness 100–1000 Å) onto a single crystal surface (Pt, Rh) [5,6]. In this way domains of varying size and geometry are created surrounded by uncovered metal surface.

3. Size-dependent reactivity and chemical waves

The PEEM images in Fig. 1 show the titration of an oxygen saturated Pt(100)/Rh microstructure with hydrogen [11]. Dark areas represent oxygen covered surface, bright areas mark a low concentration of oxygen. The two circles displayed in frame a represent Pt(100) substrate covered by oxygen. They are surrounded by an Rh layer also covered with oxygen. Initially small bright islands representing oxygen-freed area are seen to nucleate at the Pt/Rh interfaces (frame a). These islands then coalesce into closed rings which propagate outward from the

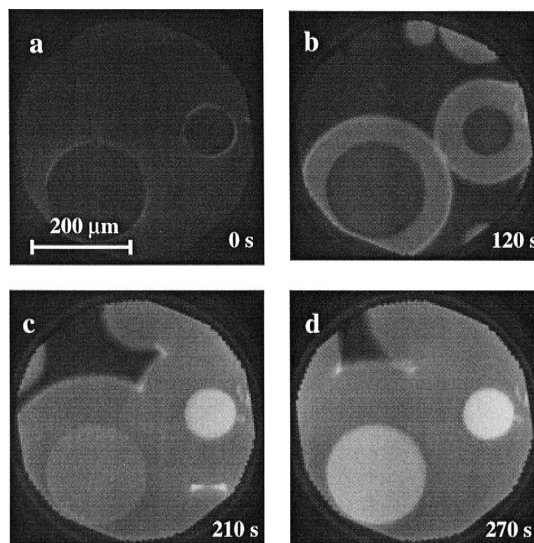


Fig. 1. PEEM images showing different stages in the titration of an oxygen saturated Pt/Rh microstructure with hydrogen at $p(\text{H}_2) = 1.5 \times 10^{-7}$ mbar and $T = 580$ K. Inside the circles, the substrate is a Pt(100) surface and the surrounding area is covered with a 500-Å-thick Rh film. The bright rings surrounding the Pt domains (frame b) are reaction fronts propagating away from the interface (from Ref. [11]).

Pt/Rh boundaries with a constant velocity of $0.45 \mu\text{m/s}$ forming perfectly circular reaction fronts (frame b), leaving behind an oxygen-freed Rh layer. Only in the final stage of this process, is the remaining oxygen inside the Pt domains completely reacted off, apparently spatially uniformly. The small domain reacts first and the larger one follows with a delay of ca. 60 s (frames c and d). This mesoscopic size effect can be rationalized in a simple way. Hydrogen adsorbing on the oxygen-freed Rh area will diffuse back into the Pt circles, at a rate roughly proportional to their perimeter, and accelerate the reactive removal of oxygen there. Since the oxygen to be reacted off is proportional to the area of the circle, the diffusional contribution will vary as $1/r$. Therefore, smaller Pt circles should react faster, in agreement with our observations.

We also investigated the influence of differently active surroundings on the reactivity of an adsorbed layer [11]. In the reaction $\text{NO} + \text{CO} \rightarrow 1/2 \text{N}_2 + \text{CO}_2$, at 300 K the surface is in its inactive state, fully covered by molecular NO/CO adsorbate; the reactivity of the Pt(100) surface at low temperature is limited by the availability of vacant sites required for the dissociation of NO [12,13]. Upon heating, however, a sharp transition (“surface explosion”) to the reactive state occurs as the combined NO/CO coverage falls below 0.5, triggering an autocatalytic increase in the number of vacant sites. On an extended Pt(100) surface this occurs via reaction fronts nucleating at some defects (scratches, etc.); on Pt(100)/Rh the reaction fronts always develop at the Pt/Rh interface.

A plot of the ignition temperature, T_{ign} , for Pt domains surrounded by Rh in Fig. 2 shows an inverse dependence of reactivity on the domain radius, r . Pt domains surrounded by a freshly cleaned Ti/TiO₂ layer (after brief sputtering) show precisely the opposite trend. No dependence of T_{ign} on the domain radius is seen after the Ti/TiO₂ layer had been in use for some time. Rh is more active in the NO + CO reac-

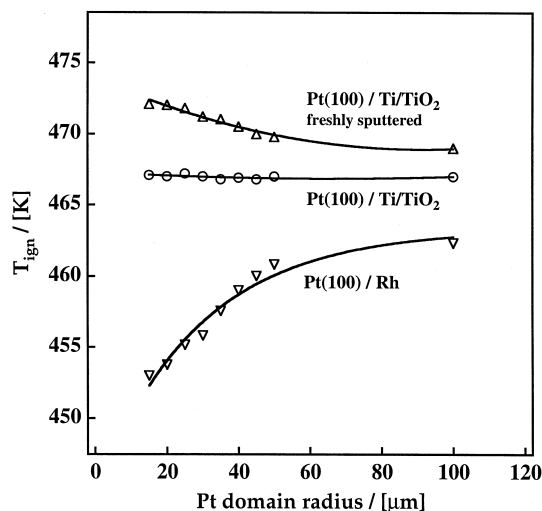


Fig. 2. Influence of the boundary conditions and of the domain size on the ignition of a molecularly adsorbed NO/CO layer on Pt(100). The plot shows the dependence of the ignition temperature, T_{ign} , on the domain radius for circular Pt(100) domains surrounded either by a reactive 500-Å Rh layer or by an unreactive 500-Å Ti/TiO₂ layer. The samples were slowly heated up in an NO/CO atmosphere starting from 300 K. Experimental conditions: $p(\text{NO}) = 1.2 \times 10^{-5}$ mbar, $p(\text{CO}) = 0.9 \times 10^{-5}$ mbar, $T = 459$ K, heating rate 0.1 K s (from Ref. [11]).

tion than Pt and therefore an outflow of both, NO and CO, across the Pt/Rh boundary will occur [8]. This decreases the NO/CO coverage in the Pt domain, thus reducing its ignition temperature. This effect will again be strongest for small domains. For an inert (zero flux) boundary, one would expect T_{ign} to be independent of r ; this is what is seen in the Ti/TiO₂ experiment. The surprising rise of T_{ign} with decreasing radius for a freshly sputtered Ti/TiO₂ layer suggests that such a boundary acts as a supplier of NO/CO.

The last examples show that domain reactivity can be modified through design of the chemical composition and the geometry of the domain boundaries. In these examples, no change of the surface composition due to alloying of the constituents, Pt and Rh, took place. If this happens, i.e., when thinner metal layers are evaporated, more complicated structures evolve as shown below.

4. Turing-like structures and adsorbate-induced segregation

We have studied the $\text{H}_2 + \text{O}_2$ reaction on a composite catalyst consisting of microstructured Pt domains on a Rh(110) surface [14]. The PEEM images in Fig. 3 show various stationary concentration patterns we observe inside the Pt domains under reaction conditions. We attribute the bright spots, which develop inside the Pt domains several minutes after the adjustment of $p(\text{O}_2)$ and $p(\text{H}_2)$, to the presence of a subsurface oxygen species, i.e., a species with a negative dipole moment [15–17]. Such a species lowers the work function, thus increasing the brightness in PEEM in contrast to the usual chemisorbed oxygen, which appears as dark area in PEEM. Remarkably, this oxygen species which is characterized by a reduced work function in PEEM only forms under reaction conditions but not in simple adsorption experiments.

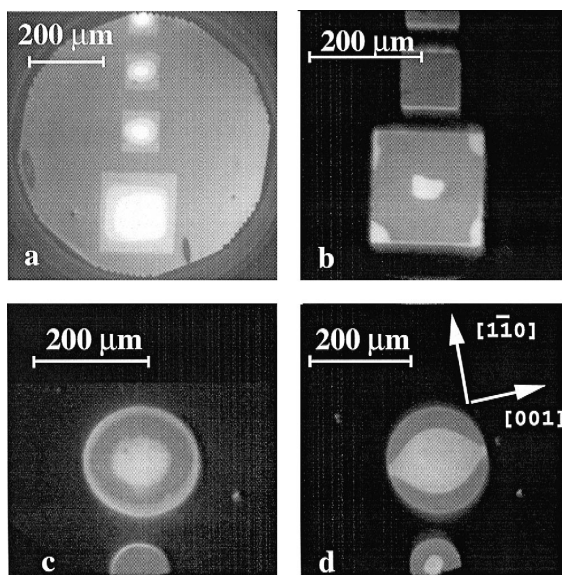


Fig. 3. PEEM images showing the formation of stationary concentration patterns during the $\text{O}_2 + \text{H}_2$ reaction on a microstructured Rh(110)/Pt surface. The squares and circles represent Pt domains surrounded by Rh(110) surface. The crystallographic directions of the Rh(110) surface are indicated for all PEEM images in (d). All images are shown with the same grey scale. Experimental conditions: $p(\text{O}_2) = 2.0 \times 10^{-6}$ mbar, $p(\text{H}_2)$: 10^{-6} mbar range, $T = 551$ K (a), 478 K (b), 526 K(c), 476 K (d) (from Ref. [14]).

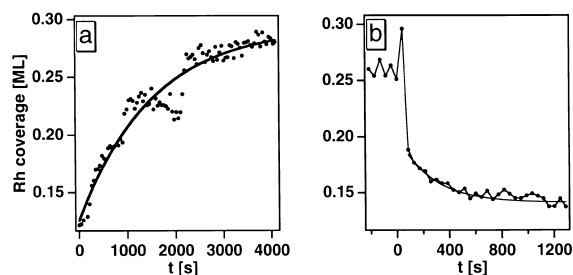


Fig. 4. The reversible segregation of Rh in a Pt domain for varying reaction conditions, i.e., conditions which correspond to (a) development of a Turing-like structure and (b) reappearance of the spatially uniform state inside the Pt domain. The Rh concentration was determined in the center of a $90 \times 90 \mu\text{m}^2$ Pt domain. Experimental conditions: $T = 600$ K, $p(\text{O}_2) = 2 \times 10^{-7}$ mbar, $p(\text{H}_2) = 1.7 \times 10^{-7}$ mbar (Ref. [14]).

(a) Formation of a bright spot in PEEM initiated at $t = 0$ by a decrease of $p\text{H}_2$ from 4.8×10^{-7} to 1.7×10^{-7} mbar. (b) Reappearance of the uniform state inside the Pt domain initiated by a $p(\text{H}_2)$ increase from 1.7×10^{-7} to 4.8×10^{-7} mbar at $t = 0$.

The formation of the stationary patterns is completely reversible and, as demonstrated by Fig. 3a–d, size- and geometry-dependent.

We can describe our composite reaction system Rh(110)/Pt/ $\text{O}_2 + \text{H}_2$ as two bistable media coupled by a fast diffusing species, atomic hydrogen [18,19]. Both metals can either be in an unreactive high oxygen coverage state or in a reactive low oxygen coverage state [20]. In order to investigate the chemistry of the system, we conducted spatially resolved chemical mapping with SPEM at ELETTRA [14]. The local photoelectron spectra taken in situ from the $90 \times 90 \mu\text{m}^2$ Pt square demonstrated that the central area not only contains oxygen but that also, rather unexpectedly, Rh is present. The Rh apparently must have segregated from the 300-Å-thick Pt film, which contains some Rh due to vertical intermixing with the Rh(110) surface underneath. The enrichment of Rh on the Pt surface is reversible and bound to the stationary patterns. The reversibility of the Rh segregation is demonstrated in Fig. 4. Fig. 4a shows that the Rh slowly segregates to the surface in ≈ 30 –40 min when we adjust reaction conditions under which a bright spot forms. Oxygen is more strongly bound to Rh than to Pt and, therefore,

adsorbed oxygen “pulls” out the Rh from a Pt film that is alloyed with some Rh [21,22]. When the pattern-forming parameter range is left, a Pt surface with the low Rh concentration initially present is established again within ca. 10 min as demonstrated by Fig. 4b. The slow time scale can be attributed to the vertical diffusion of Rh in the Pt layer. The Rh surface concentration in these experiments varies between $\theta_{\text{Rh}} = 0.29$ and $\theta_{\text{Rh}} = 0.04$.

The existence of stationary concentration patterns in a chemical reaction system has been predicted more than 40 years ago in a pioneering paper by A. Turing [23]. Turing patterns typically form in an RD system when a fast diffusing inhibitor and a slow diffusing activator species are both present. Since the domain boundaries are of obvious importance for the development of the patterns, (whereas a Turing pattern possesses an intrinsic wavelength) we denote them as Turing-like structures. The mechanistic understanding is still rather incomplete. In particular, the role of potassium, which was present as contaminant, needs to be clarified.

The above example demonstrates that diffusion instabilities in catalytic surface reactions may give rise to a spatially modulated composition of alloyed surfaces. In these Turing-like patterns, the catalyst itself is a dissipative structure, changing its composition in response to varying parameters. The results show that a purely static analysis in terms of a fixed surface composition and surface structure does not suffice to understand the functioning of real catalysts.

5. Mathematical modeling

Simulations of reactions on composite surfaces have initially been conducted for catalytic CO oxidation focusing on the effect of geometry and size restrictions for the system Pt(110)/CO + O₂ [5,6]. Recent calculations that were carried out for the NO + H₂ reaction on a com-

posite Pt/Rh surface were able to reproduce the experimentally observed effects quite well [24,25]. They demonstrated that the dynamic behavior of such composite surfaces is dominated by reaction fronts initiated at the Pt/Rh interface.

6. Conclusions

It was shown that a fast diffusing species like hydrogen can lead to dynamic coupling effects over macroscopic distances effects, which can also decisively affect the integral behavior of a catalyst. Controlled front nucleation at domain interfaces was likewise demonstrated. Since these effects are size-dependent, they can be controlled by appropriately designed composite surfaces. While the economic use of such catalysts may still lie far ahead in the future, the study of such systems provides us with the unique opportunity to systematically investigate dynamic effects in catalysis — a possibility that would be rather difficult to realize with real catalysts.

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