



Non-equilibrium surface pattern formation during catalytic reactions with nanoscale resolution: Investigations of the electric field influence[☆]

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ABSTRACT

The present paper overviews our recent experimental and theoretical results concerning the catalytic properties of nanosized rhodium and platinum facets in the presence of an external electric field. We first show that field ion microscopy (FIM) experiments along with corresponding density functional theory (DFT) calculations strongly indicate that a positive field value promotes the oxidation of a rhodium field emitter tip. We also demonstrate that the catalytic oscillatory nanopatterns, as observed when H₂ and O₂ are exposed on a rhodium field emitter tip, find their origin in the different catalytic properties of all the nanofacets that are simultaneously exposed at the tip's surface. In the case of platinum field emitter tips, the dependence of dissociation barrier of NO on the external electric field is examined with DFT and compared to experimental results. Corresponding calculations on Pt are done for the (NO)₂ dimer.

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1. Introduction

Heterogeneous catalysis by metals plays an important role in modern industrial chemistry to ensure technical progress along with sustainability. With this background it comes as a surprise that many catalytic reactions deemed to be simple have a detailed mechanism and underlying kinetics that are still unknown. While it has become clear over the years that molecules on solid metal surfaces hardly move like checkers on a checkerboard the diversity of phenomena ranging from bistability and kinetic oscillations to spatio-temporal patterns is remarkable [1–4]. To provide a sound understanding of these phenomena, surface science techniques may be employed in studies with oriented 2D single crystals [1,3,4]. However, it has been recognized that a 2D sample is morphologically an oversimplification as compared to the 3D nanosized particles usually applied in heterogeneous catalysis. Such particles are multifaceted and deposited at high dispersion on an oxide support. This difference in morphology and compositional complexity constitutes the so-called materials gap. To approximate the 3D morphology of a single nanometer-sized metal particle, in the absence of an oxide support, the apex of a field emitter tip can be considered a most suitable approach. In fact, near-atomic resolu-

tion of the tip can be achieved under the operating conditions of a field ion microscope (FIM) where an external electric field of the order of 10 V/nm is applied to either image the surface structure at low temperatures or reacting adsorbates at higher temperatures. Moreover, the field ion microscope allows studying the cooperative effects in a nonlinear chemical reaction since a large number of nanosized facets are simultaneously exposed at the surface of a 3D tip [5]. The present article is dedicated to Ben Nieuwenhuys, who has made many important contributions to understanding nonlinear catalytic surface science by using the field electron microscope [6–8].

In this paper, we will summarize our recent work that we have done by using the field ion microscope along with local chemical probing of single facets of 3D field emitter tips. We first address the catalytic formation of water from oxygen and hydrogen, which is one of the very first systems that has been studied in the framework of heterogeneous catalysis, some 150 years ago [9–11]. Despite its apparent simplicity, the underlying mechanism is still the subject of numerous investigations [12]. Recently, this reaction has received a considerable amount of attention since a surface oxide seems to form during the reaction over rhodium surfaces [13–18]. One of the underlying concerns is the correlation of the catalytic activity with the formation of this oxide layer. Interestingly, the modeling of the surface oxide in a trilayer configuration turns out to be a promising approximation susceptible to reach this goal [19,20]. On field emitter tips, a number of studies have also been reported, but an understanding of the origin of the oscillating nanopatterns has been lacking until recently [5,21]. Using the experimental and

[☆] In honor of Ben Nieuwenhuys.

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theoretical tools of Sections 2 and 3, we present in Section 4 our work on rhodium field emitter tips when they are exposed to H_2 and O_2 [22,23]. In particular, *ab initio* calculations on adsorbates in the presence of an external electric field will be described and a corresponding kinetic model of the bistability and the kinetic oscillations, as observed experimentally by video-field ion microscopy, will be presented. In this manner we shall demonstrate that the electric field acts at overall low pressures in a similar way as high pressures do in the absence of an electric field. While usually the formation of a surface oxide layer under UHV conditions may not be thermodynamically expected, the presence of an electric field can render it possible.

A nonlinear behavior is also observed when a platinum field emitter tip is exposed to H_2 and NO or NO_2 . From the theoretical point of view, such a system with a heteronuclear molecule turns out to be even more complex as compared to the former case in which only homonuclear molecules react to form a single product molecule. In Section 5 we will present nonlinear reaction phenomena along with some new calculations involving the dissociation of NO on a stepped platinum surface. This dissociation is known to play a key role in the overall reaction mechanism and depends strongly on the local surface geometry. An interesting aspect here is the strong influence of the electric field on the reaction behavior. The interesting point for heterogeneous catalysis is that electric fields of this magnitude are comparable to those related to alkaline and earth-alkaline promoters or “simply” metal–metal oxide interfaces. Relatively low fields of several V/nm can be met in scanning tunneling microscopy (STM) measurements as well and have turned out to be sufficient to produce N_2O from NO on Pt field emitter tips at field strengths of several V/nm [24]. The N_2O formation under realistic conditions of heterogeneous catalysis is a well-known (and unwanted) phenomenon occurring on a number of different catalyst materials. More specifically, the influence of coadsorbed potassium on the NO adsorption and decomposition behavior is well documented in the literature [25].

2. Experimental setups

Two different setups were used for the experimental studies reported in this paper, which are briefly overviewed here. A detailed description of both setups can be found elsewhere [26]. In the first setup, the field ion microscope was used as a flow reactor to image, with nanometric resolution, the ongoing catalytic reactions that occur at the surface of a field emitter tip. A resolution of 2–3 Å can be obtained at cryogenic temperature conditions using an inert gas, helium or neon, as the imaging species. An example of such atomic resolution capabilities can be seen in Fig. 1. To follow the dynamics of a catalytic surface reaction, the noble gas is replaced by a flow of reactant molecules with appropriate partial pressures and a temperature sufficiently high to cause a reaction to occur. This eventually results in the observation of dynamic reaction phenomena with nanoscale lateral resolution. Rhodium or the platinum field emitter tips serving as catalyst samples are first conditioned by several cycles of field evaporation, noble gas sputtering and heat treatment before subjecting them to reaction studies. Clean tips are used as a reference to calculate the value of the field strength. The tip's radius of curvature is calculated by counting the number of atomic layers between two facets of known orientation. Standard FIM images are taken with a high dynamic range Roper Scientific CCD camera (512 × 512 pixels, 16 bits per pixel). For dynamic reaction imaging, a high sensitivity video camera with a time resolution of 20 ms is employed. Local brightnesses are then evaluated by pixel analysis of the digitized data.

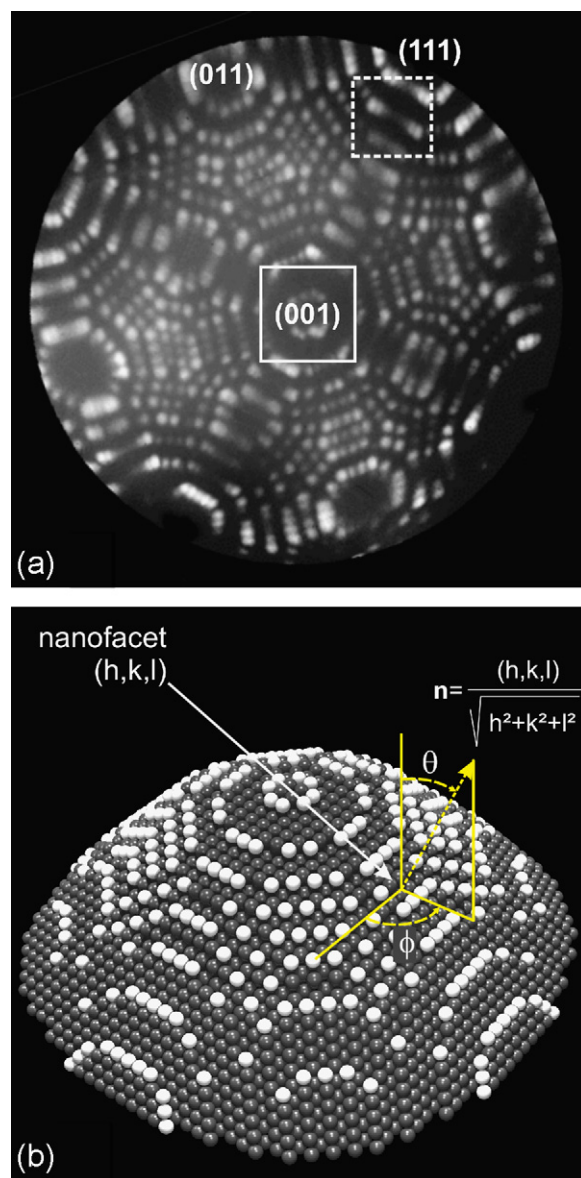


Fig. 1. (a) Field ion micrographs of a clean (001)-oriented Rh tip imaged by neon at $P_{Ne} = 10^{-3}$ Pa, $T = 55$ K, $F \sim 35$ V nm $^{-1}$. The radius of curvature is about 10 nm. (b) Ball model of the field emitter tip with the unit vector $\mathbf{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ perpendicular to the nanofacet of Miller indices (hkl) of an underlying fcc crystal. All the balls inside a paraboloid are retained in this model of the field emitter. We notice that the mean electric field points in the same direction $\mathbf{F} = F\mathbf{n}$ because the electric field is always perpendicular to the surface of a conductor such as the field emitter tip.

In a second setup, pulsed field desorption mass spectrometry (PFDMS) allows a chemical identification of adsorbed layers during the ongoing catalytic reaction. To do so, field pulses (~ 100 ns width) are applied to a counter electrode (with a hole) in front of the rhodium tip. Pulses rupture species as ions which pass the probe hole of the microscope screen and enter a time-of-flight mass spectrometer for chemical identification. Pulse amplitudes may vary and can be adjusted such that the dynamics of a catalytic reaction are visibly not influenced. On the other hand, field pulse amplitudes may be high so as to ensure quantitative field desorption and to determine surface coverages. A “reaction field” can be maintained between pulses. Varying this field provides insight into the field dependence of adsorption and reaction processes.

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