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Field emission techniques for studying surface reactions: Applying them to NO–H_2 interaction with Pd tips

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ABSTRACT

The adsorption of NO and its reaction with H_2 over Pd tips were investigated by means of field ion microscopy (FIM) and pulsed field desorption mass spectrometry (PFDMS) in the 10^{-3} Pa pressure range and at sample temperatures between 400 and 600 K. By varying the H_2 partial pressure while keeping the other control parameters constant, the NO+H_2 reaction over Pd crystallites is shown to exhibit a strong hysteresis effect. The hysteresis region narrows with increase in temperature and the H_2 pressures delimiting this hysteresis decrease as well. Abrupt transformations of the micrographs are observed by FIM from bright to dark patterns and vice versa. These transformations define the hysteresis region. The collected data allow establishing a novel kinetic phase diagram of the NO+H_2/Pd system within the range of temperatures and pressures indicated. The observed features are correlated with a local chemical analysis by means of field pulses. NO^+ seems to be the dominating imaging species under all conditions. At high relative H_2 pressures (the "hydrogen-side"), H atoms seem to diffuse subsurface. This process is blocked at lower H_2 pressure (the "NO-side") due to NO_{ad} and O_{ad} accumulation on the surface. Probe-hole measurements with field pulses indicate that the Pd surface undergoes oxidation as revealed by the occurrence of PdO_2^+ species in the mass spectra.

1. Introduction

Since the mid-1990s, Block and his group have focussed their research on demonstrating the relevance of using field emission techniques to study dynamic reaction phenomena on the surface of field emitter tips. Using video-field electron microscopy they were able to make visible wave fronts in simple catalytic reactions like the CO oxidation [1]. The phenomena eventually resulted in self-sustained oscillations. Shortly after, video-field ion microscopy was applied to the same reaction at somewhat different reaction pressures and temperatures. As one of the highlights of these combined FEM/FIM research works, cross-shaped kinetic phase diagrams were published with similarities to measurements on extended single crystal surfaces in the absence of high electric fields [2,3]. Other reactions like the water formation from O_2+H_2 or the NO reduction with H_2 were subsequently studied using video-FEM/FIM along with atom-probe techniques to elucidate the surface composition and the chemical nature of the reaction intermediates [4–6]. In most of these studies Pt and Rh emitter tips were used as model catalysts. This choice is explained by the importance of these metals as catalysts in converters of automotive vehicles. All the above reactions play a role whatever the abatement strategy and a very high level of pollution control for CO, unburnt hydrocarbons and NO_x is obtained under stoichiometric air-to-fuel conditions [7]. Lean-burn driving conditions with gasoline and diesel engines yet remain a concern with respect to the reduction of NO_x [8]. Despite major efforts in developing alternative technologies, fuel-powered vehicles will continue to dominate the normal street scene for many years. It is thus obvious that heterogeneous catalysis remains the primary focus for controlling and decreasing pollutant emissions, and a thorough understanding of the ongoing surface processes can be obtained by surface science and, in particular, by field emission techniques. These questions, amongst others, were intensively studied by Block and his group, whose seminal contributions using field emission techniques still inspire a number of research groups, including ours. Real catalyst particles are a dispersion of nanometre-sized crystallites, exposing many crystal facets, steps, kinks and defects. In field emission techniques, the highest achievable working pressure is of the order of several 10^{-2} Pa and the sample is conditioned as a well-characterized sharp tip. Therefore, an important pressure and materials gap exists between conventional experiments and practice. However, in contrast to scanning tunnelling (STM) and atomic force microscopies (AFM), the hemispherical specimen apex closely approximates the spherical metal particles in a real catalyst both in shape and scale, thus reducing to some extent the materials gap. As for the exhaust converter, one can use the main chamber of a field emission/ion microscope as a

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flow reactor with a constant supply of reactants. Under these conditions, far from the thermodynamic equilibrium, temporal and spatial self-organization become possible [9] along with the emergence of bistability when external control parameters (partial pressures, temperature and electric field) are changed. Reviews on the applications of field emission techniques for heterogeneous catalysis studies have been published more recently with emphasis on the influence of the external electric field on the surface processes [10–12].

In the present paper, we focus on the NO reduction with hydrogen on Pd tips using video-FIM and atom probe techniques under dynamic imaging conditions. Structural transformations and non-linearities at the surface of a Pd tip are presented along with simultaneous local chemical analysis.

2. Experimental

Two different set-ups were used for the studies reported here. The field ion microscope (FIM) was described in detail elsewhere [13] and the principles of the pulsed field desorption mass spectrometry (PFDMS) instrument were already described by Block in 1975 [14]. Some of its basic features have been taken over and integrated in a newer version available in Brussels [15].

The FIM was used either for studies of surface structures before and after exposure to reactive gases or for in-situ studies of dynamic surface reactions. The PFDMS instrument was used to reveal the surface composition with nanometric lateral resolution while imaging. To do so, electric field pulses ($F < 50\ V\ nm^{-1}$, widths > 100–400 ns, frequency < 10 kHz) were applied to a counter electrode with a hole placed in front (~0.1–1 mm) of the tip specimen. Standard field ion micrographs were taken by a highly sensitive, back-illuminated, charge-coupled device camera (Princeton Instruments VersArray 512B-XP, 512×512 pixels, 16 bits dynamic resolution) whereas video-FIM was achieved by means of a moonlight video camera with a time resolution of 20 ms.

Palladium tip samples were produced by electrochemical etching in a suspended drop of 10% aqueous solution of KCN at 3 V dc. High purity wires of 0.1 mm diameter were provided by Advent Research Materials. Because of the very long durations necessary for etching – several tens of minutes – we designed the cathode so as to avoid the perturbation of the regular etching by the bubbles produced in the droplet (see Ref. [16] for details).

Neon gas was used as imaging gas at a field of $35\ V\ nm^{-1}$ and 55 K to produce atomic resolution of the field emitter tips such as those presented in Fig. 1. The micrograph was obtained after a moderate treatment by field evaporation and is put in comparison with a face-centered cubic ball model as a guide to the eye. Such high-resolution micrographs usually serve as a starting point for catalysis studies at higher temperatures (< 600 K) with somewhat lower field strengths ($< 12\ V\ nm^{-1}$). Under these conditions chemically reacting molecules – and for some cases reaction products – can serve as imaging species with a reduced lateral resolution.

3. Results and discussion

3.1. Bistability during NO+H_2 interaction over Pd tips

The reaction experiments were performed in the following manner. First, the tip temperature was raised to values of interest (~400–600 K). Then NO was introduced at pressures ranging from 10^{-4} to 10^{-2} Pa. After pressure equilibration, an electric field of about $10\ V\ nm^{-1}$ was applied, sufficient for field ionization and image formation to occur. Finally, hydrogen was slowly introduced into the microscope chamber at pressures between 10^{-4} and 10^{-2} Pa while continuously monitoring the pattern sequences using the video system. Fig. 2 shows a set of four micrographs obtained from a video sequence after introducing a NO/H_2 gas mixture (partial pressure 10^{-3} Pa each) into the microscope

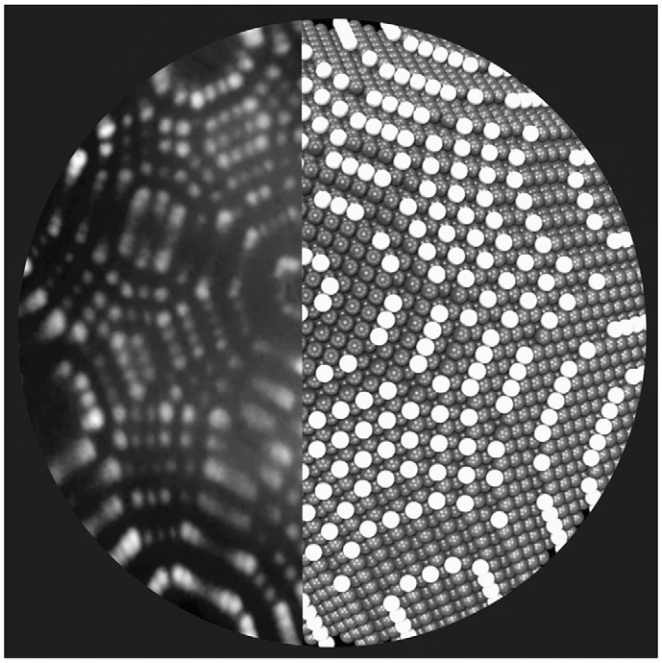

Fig. 1. High resolution field ion micrograph of an FCC-metal tip along with a ball model constructed with a close to 1:1 scale.

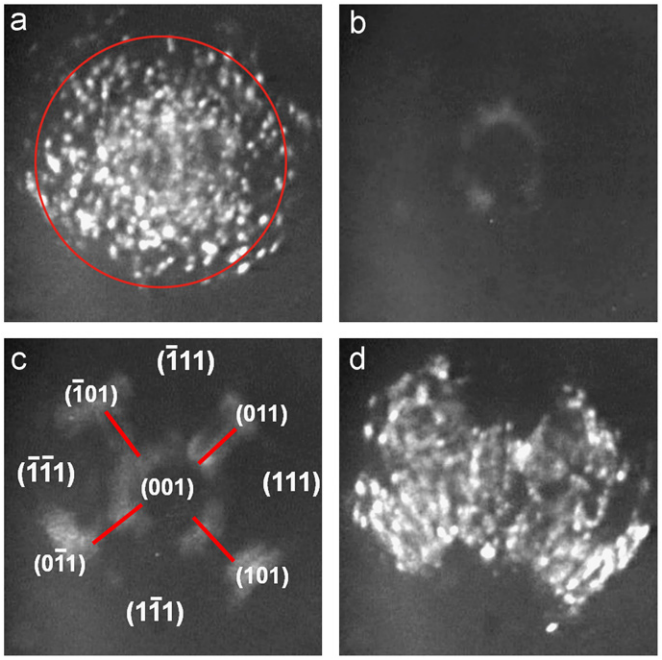

Fig. 2. (a) FIM pattern during the NO/H_2 interaction over a Pd tip ; reaction conditions: T=450 K, $p_{NO}=P_{H_2}=10^{-3}$ Pa. The features of the pattern indicate the occurrence of surface oxidation following NO dissociation. (b) Abrupt darkening of the pattern encountered in (a) when the hydrogen pressure is increased to 3.5×10^{-3} Pa, indicating the occurrence of a fast reaction between O_{ad} and H_{ad}. (c) FIM during the decrease of the hydrogen pressure below 3.5×10^{-3} Pa ($p_{H_2}=2 \times 10^{-3}$ Pa) with some Miller indices indicating the symmetry of the tip apex. (d) Recovery of a FIM pattern similar to that of (a) when p_{H_2} is further decreased to 10^{-3} Pa.