Regular and irregular spatial patterns in the catalytic reduction of NO with NH₃ on Pt(100)

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The catalytic reduction of NO with NH₃ on a Pt(100) surface, which exhibits kinetic oscillations under isothermal conditions in the 10⁻⁶ mbar pressure range, has been studied by photoemission electron microscopy (PEEM) as a spatially resolved technique. Oscillations in the rate of product formation for N₂ and H₂O are observed between 425 and 450 K. During the rate oscillations, the surface reacts predominantly spatially uniformly. Towards the lower T-boundary for oscillations, however, fluctuating adsorbate islands (diameter ≈ 10–50 μm) appear and one observes target patterns and rotating spirals. Below the lower T-boundary for oscillations, the reaction rate is stationary, but with PEEM one observes a spatially chaotic pattern in which the surface is still oscillating locally. The transition from macroscopic rate oscillations to unsynchronized oscillatory behavior can be associated with the breakdown of long range synchronization via gas phase coupling. In the spatial patterns imaged by PEEM, one can clearly identify three distinct grey levels which undergo a cyclic transformation into each other via propagating reaction fronts. One can assign different mechanistic steps to these transformations, namely the lifting of the hex reconstruction through NO adsorption and the dissociation of NO on the 1×1 phase, decomposition of NH₃ on the 1×1 O_ad/NO_ad phase, and the restoration of the hex surface.

Keywords: Catalytic NO reduction; kinetic oscillations; spatial pattern formation; chemical turbulence

1. Introduction

Spatially resolved measurements during kinetic oscillations have revealed that the variations in the reaction rate are associated with spatially and temporally varying concentration patterns on the catalyst surface [1,2]. Most of these investigations have been performed under isothermal conditions at low pressure (p < 10⁻³ mbar) on single crystal surfaces where the newly developed photoemission electron microscope (PEEM) demonstrated a spectacular variety of different spatiotemporal patterns [3–5]. In this paper, we report the results of PEEM measurements in the NO + NH₃ reaction on Pt(100) whose oscillatory behavior has been investigated earlier [6–8].
This work is part of an ongoing investigation in which we have studied the oscillatory behavior of the NO reduction with the reactants CO [5,9], H₂ [10] and NH₃ [6,7] on a Pt(100) surface at low pressure (10⁻⁶ mbar). All these systems exhibit similar dynamical behavior whose origin presumably lies in the requirement of vacant sites for NO dissociation which is the rate-limiting reaction step:

\[ \text{NO}_{\text{ad}} + * \rightarrow \text{N}_{\text{ad}} + \text{O}_{\text{ad}}, \]

where * denotes a vacant site. Since more vacant sites are liberated in the subsequent product forming steps than are consumed by the above step, autocatalytic behavior results. In all three NO + X reactions (X = CO, H₂, NH₃) on Pt(100), the autocatalysis manifests itself by the occurrence of extremely narrow product peaks at \( T \approx 400 \) K in temperature programmed reaction (TPR) studies [11,12]. This effect has been referred to as “surface explosion”.

Although one can suspect that in the NO + NH₃ reaction the “surface explosion” plays a similar key role in the oscillatory mechanism as in the NO + CO reaction, which has been analyzed in depth previously [9,12], the picture is rather complicated in the present case. As will be shown in this report, in PEEM we observe spatial patterns with a characteristic sequence of transformations which we can associate with different steps of the overall mechanism. Thus, the results of spatially resolved measurements can help to clarify a complicated catalytic mechanism.

2. Experimental

The experiments were conducted in a standard UHV system of 80 ℓ volume which was operated as a gradient free flow reactor, continuously pumped by a 360 ℓ/s turbomolecular pump (effective pumping rate \( \approx 100 \) ℓ/s). For rate measurements, a differentially pumped quadrupole mass spectrometer (QMS) was attached to the chamber. During PEEM measurements, UV light from a deuterium discharge lamp with a maximum emission between 5.2 and 6.2 eV photon energy was focused onto the sample into a small spot (\( \approx 1 \) mm²) [13]. The emitted photoelectrons from the sample were focused by the electrostatic three lens system of the PEEM, amplified by a channel-plate electron multiplier, and then imaged onto a phosphorous screen. These images were then recorded with a CCD camera and stored on a video tape. The Pt(100) sample, which was of the dimensions \( \approx 5 \times 5 \) mm² and \( \approx 1 \) mm thickness, was cleaned by standard methods involving repeated cycles of oxidation and Ar ion sputtering. For the experiments, high purity gases were used (NO 99.8%, NH₃ 99.7%) which were introduced into the chamber via leak valves. All PEEM images shown were recorded with the same magnification such that the width of the