



## Modeling ammonia oxidation over a Pt (533) surface

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### ABSTRACT

We present a new reaction model for ammonia oxidation on a Pt (533) surface and perform numerical simulations using mean field equations. Kinetic parameters were taken from experiments and Density Functional Theory (DFT) calculations. The model is based on an oxygen-activated ammonia decomposition and includes  $\text{NH}_x$  ( $x=0, 1, 2$ ) intermediates. Reaction rates and coverages obtained from calculations show semiquantitative agreement with values from kinetic and in-situ XPS measurements up to 0.1 mbar pressures. Pathways for ammonia oxidation were analyzed by varying kinetic parameters in the model, which provides new insights into the relative importance of different reaction steps.

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### 1. Introduction

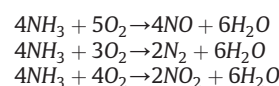
The selective oxidation of ammonia with air over Pt/Rh catalysts to NO in the so-called Ostwald process is one of the most important catalytic processes in chemical industry. In environmental catalysis the oxidation of ammonia to nitrogen is a key step in removing air pollutants in the so-called selective catalytic reduction (SCR) process [1]. With regard to the significance of catalytic ammonia oxidation it is quite surprising that relatively few mechanistic and kinetic studies have been performed. The lack of interest in a precise modeling of ammonia oxidation can be traced back to the fact that under the conditions of the Ostwald process ( $T > 900$  K) the production of NO is limited by mass transport to the surface and not by surface processes. Over the past ten years a number of microkinetic models have been proposed which all rely on the assumption that ammonia decomposition on platinum is activated through direct interaction of ammonia with chemisorbed oxygen or OH species, whereas non-activated decomposition of ammonia plays a negligible role [2–6]. These models are all quite similar and they all succeed in reproducing the main qualitative features of the experiment. What is missing in these simulations is a detailed comparison with experimental data, in

particular, with respect to a quantification of adsorbate coverages and with respect to the structure sensitivity of the reaction. Providing such a detailed comparison is the aim of this paper.

Single crystal studies of ammonia oxidation have been conducted with Pt (100), Pt (111) and with various stepped and kinked Pt (111) surfaces [7–15]. Most of these studies were performed at low pressure, in the range from  $10^{-9}$  to  $10^{-4}$  mbar. In an attempt to bridge the so-called pressure gap, the reaction studies were extended up to 0.1 mbar for various orientations [16,17]. To circumvent heat and mass transport problems, investigations with supported Pt and with monolithic polycrystalline Pt were conducted in microreactors [18].

On the theoretical side ammonia decomposition and the interaction of ammonia with oxygen was studied with DFT (density functional theory) calculations for Pt (111), Pt (100), and Pt (211) [19–23]. Both, the experimental as well as the theoretical studies agree that ammonia decomposition is activated by adsorbed oxygen or OH. The alternative pathway of first decomposing ammonia on a bare Pt surface followed by recombination of the fragments with oxygen and OH, plays a negligible role under typical experimental conditions.

Possible products in ammonia oxidation are  $\text{N}_2$ , NO,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$  as reflected by the following reaction equations:



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The availability of oxygen controls the competition between  $N_2$  vs. NO formation. A large  $O_2/NH_3$  ratio and a high temperature favour NO formation, whereas at low temperatures and low  $O_2/NH_3$  ratios  $N_2$  is the preferred reaction channel.  $N_2O$  is a byproduct which is formed in significant amounts only at higher pressure ( $>10^{-2}$  mbar). Due to the disastrous effect on global warming,  $N_2O$  formation is an undesired byproduct.

Experiments in which Ar and He were added as inert gas showed that at  $p=30\text{--}60$  mbar and  $T=523$  K mass transport limitations become significant above 660 K [7]. Unless a model takes explicitly mass and heat transport into account, which means solving the Navier–Stokes equations for the reactor, a simulation is meaningful only up to  $10^{-1}$  mbar. A full reactor model was used by Rebrov et al. [24,25] to simulate ammonia oxidation over Pt/ $Al_2O_3$  in microreactor at pressures close to 1 bar. Scheibe et al. [2] formulated a model specifically aimed at describing ammonia oxidation over the stepped Pt single crystal surfaces, Pt (533) and Pt (433). Kraehnert and Baerns [18] in their model, simulated ammonia oxidation over a Pt foil in a microstructured reactor at pressures  $<6 \times 10^{-2}$  mbar. All these models are rather similar in the sense that oxygen activates ammonia decomposition. The oxygen-activated decomposition is lumped into one step while  $NH_x$  ( $x=1, 2$ ) intermediates as well as hypothetical oxygen containing  $NH_xO_y$  intermediates are not considered.

The reason to neglect decomposition intermediates was that the corresponding kinetic parameters were not available at that time. Only when DFT calculations yielded reaction profiles for the complete pathways of OH- and O-assisted ammonia decomposition in Pt (111), Pt (100) and Pt (211), the missing kinetic constants became accessible. With in situ XPS, the adsorbate coverages during ammonia oxidation over Pt (533) have been followed at two different pressure ranges,  $10^{-4}$  mbar and at  $10^{-1}$  mbar [17].

In this study we chose Pt (533) as model system because, in addition to the XPS experiments, kinetics of ammonia oxidation have been studied over a vast pressure range from  $10^{-6}$  to  $10^{-2}$  mbar [26,27]. Stepped Pt (111) surfaces can be considered as model system for a real, that is polycrystalline, Pt catalyst. A flat Pt (111) surface is not a good model system because (due to a low  $O_2$  sticking probability) will exhibit low catalytic activity [28]. The unreconstructed Pt (100) surface exhibits also a high catalytic activity but compared to stepped Pt (111) surfaces, this orientation has the additional complication of an adsorbate-induced surface reconstruction [29,30].

The main motivation to study the kinetics of ammonia oxidation on Pt (533) over a vast pressure range was to bridge the so-called pressure gap in heterogeneous catalysis. The Ostwald process is conducted at atmospheric pressure. At elevated pressures an oxidation of the Pt catalyst might take place, but up to nearly 1 mbar no signs of any oxide formation were found in XPS [17]. Another complication is the reaction-induced restructuring of the Pt catalyst [31,32]. In the Ostwald process, the Pt/Rh gauze becomes visibly roughened already during the first minutes of operation. The extent of reaction-induced restructuring is dependent on the total pressure but also under the mild conditions of an experiment in an UHV environment the Pt surface is modified by the reaction. On Pt (533) at pressures beyond  $1 \times 10^{-4}$  mbar a reversible doubling of the step height occurred under certain reaction conditions [22,26]. Since the effect is pressure dependent, reaction-induced restructuring is part of the pressure as well of the material gap.

In the simulations here presented, the catalyst was treated as rigid surface; that is, we neglect dynamic restructuring effects caused by the surface reaction. As will be shown, with this approach we achieve a semi-quantitative modeling of the kinetics. The results provide us with insights into the pathways of ammonia oxidation, essentially confirming the importance of the oxygen activated ammonia decomposition.

## 2. The model

### 2.1. The reaction mechanism and mathematical equations

The model describes the reaction under isothermal conditions with heat and mass transport limitations playing no role. The

conversion rate is assumed to be small so that readsorption of products is negligible. The surface is considered as rigid, i.e. reaction-induced restructuring effects do not exist.

The Pt (533) surface also written as  $4(111) \times (100)$  consists of 4 lattice units wide (111) terraces, separated from each other by a step with (100) orientation, as demonstrated by the structural model of Pt (533) in Fig. 1. Since at least two reaction steps,  $O_2$  adsorption and NO decomposition are known to be highly structure sensitive, the question is how to describe the behavior of the Pt (533) surface which is composed of (100) and (111) facets. NO-decomposition/NO-formation should be restricted to the (100) step sites, whereas the (111) terrace sites should be fairly inactive [33–36]. In the model, we do not formulate separate equations for the step and for the terrace sites but we homogenize the surface. Through the choice of the constants we can, however, take into account that the (100) steps govern the catalytic activity of Pt (533) for certain reaction steps. The various adsorbates occupy different adsorption sites on Pt (100) and Pt (111) but in the model we assume a single adsorption site. So-called dual-adsorption sites models have been proposed [24]; the underlying assumption of two adsorption sites which can be populated completely independent of each other is, however, unphysical because energetic interactions or site blocking by steric effects will in any case cause dependence [37].

Transforming the set reaction equations R1–R13a into kinetic equations, we arrive to a set of 7th-order coupled ordinary differential equations (ODE's) plus one independent expression for the amount of free sites. Eqs. (1)–(8) describe the variation of the surface coverages of O, OH,  $NH_x$ , ( $x=0\text{--}3$ ), NO, and vacant sites (symbolized as \* with coverage  $\theta_*$ ):

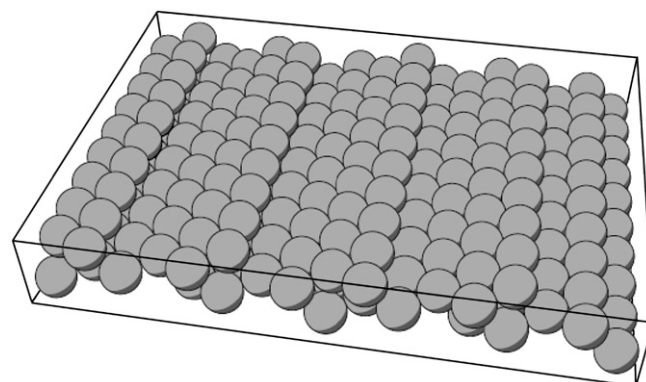
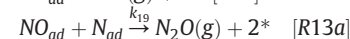
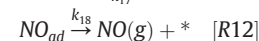
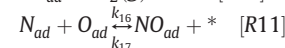
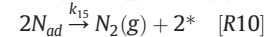
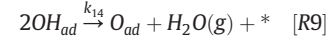
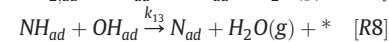
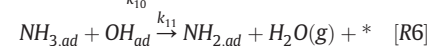
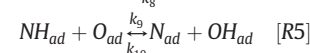
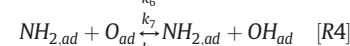
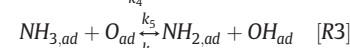
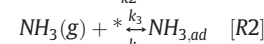
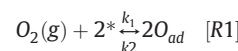


Fig. 1. Ball model of the Pt (533) surface.

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