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The O_2 + NH_3 Reaction Over Rh(110): Steady State Kinetics and Oscillatory Behavior

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Abstract The kinetics of ammonia oxidation with oxygen over a Rh(110) surface were studied in the pressure range 10^{-5}–10^{-4} mbar. Nitrogen was found to be the preferred product at low partial pressures ratios $p_{o_2} : p_{NH_3}$, while the NO pathway was favored with oxygen rich gas mixtures and at high temperature. The reactive sticking coefficient of O_2 reaches up to 0.05 under steady state conditions. Pronounced hysteresis effects in the reaction rates were found in T-cycling experiments. Sustained oscillations in the reaction rates occurred under isothermal conditions at $T = 620$ K at a total pressure of 4×10^{-5} mbar.

Keywords Rhodium · $NH_3 + O_2$ reaction · Kinetic oscillations · Single crystal

1 Introduction

Quite a number of surface science studies investigated in recent years the catalytic ammonia oxidation with O_2 over various d-band metal catalysts such as Pt, Pd, Ir, Ru, and Rh [1–11]. The experimental investigations were accompanied by quantum chemical calculations conducted mostly with the density functional theory (DFT) [12, 13]. These studies were in part motivated by the industrial importance of the so-called Ostwald process which is essential for producing nitric acid, and in part by the need in environmental chemistry to remove ammonia from tail gases [14, 15]. Very few studies of the $O_2 + NH_3$ reaction have been carried out using Rh surfaces as catalyst, despite the fact that not pure Pt but Pt/Rh alloys are typically used as gauze in the Ostwald process. Pérez-Ramírez et al. [6] experimentally studied the high-temperature ammonia oxidation (relevant for industrial applications) on Pt, Pd, and Rh polycrystalline wires via the temporal analysis of products (TAP) technique [7]. The typical order for selectivity towards the desired product in the Ostwald process (NO formation), Pt > Pd > Rh was rationalized by these authors taking into account that nitric oxide loss reactions become more favored on Rh, thus leading to an increase of side products such as N_2O. Additionally, high oxygen fractions in the reactant mixture (and therefore higher coverages) were also found to cause an enhancement of NO selectivity via suppression of dissociation reactions. For closely related system, such as the ammonia reaction with NO over polycrystalline Pt foil, oscillations in the reaction rates for temperatures between 600 and 670 K and pressures in the mbar range were reported in the past (see Ref. [8–11] and references therein).

The kinetics of ammonia decomposition were investigated on various Rh single crystal surfaces [16, 17]. The titration of the oxygen covered Rh(110) surface with ammonia has been followed with scanning tunneling microscopy [18]. Due its enormous structural variability the Rh(110) surface has been intensely studied in the recent years, focusing on the various oxygen- and nitrogen-induced reconstructions [19], Fig. 1 shows a schematic ball model of the surface. This structural variability is also responsible for interesting nonlinear dynamics of the

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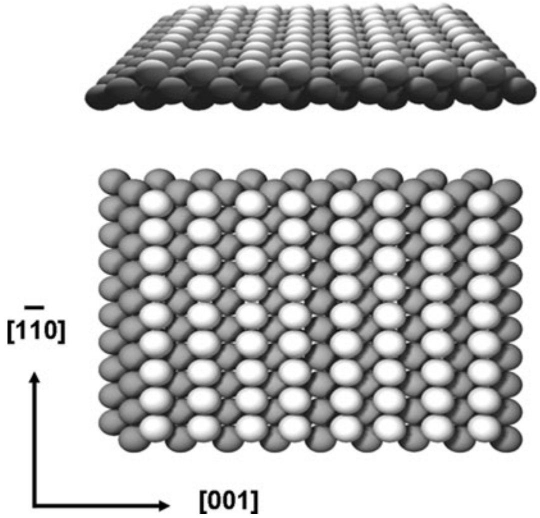

Fig. 1 Ball model of the fcc (110) surface structure

$NO + H_2$ reaction on Rh(110). Rate oscillations and a large variety of unusual chemical wave patterns were found in this system [20–22].

In this article we report on the kinetics of ammonia oxidation on Rh(110) which we studied in the 10^{-6}–10^{-3} mbar range, using mass spectrometry and measurements of the reactive sticking coefficient. Ammonia reacts with oxygen to form the main products N_2, NO, and H_2O [1–3]. On Pt at elevated pressures ($p > 10^{-2}$ mbar) a minor amount of N_2O is also formed during ammonia oxidation [23]. The main reactions pathways are the following:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O.$$

We find rate hystereses in heating/cooling cycles and oscillatory behavior. Spatially resolved measurements reported elsewhere show that novel types of chemical wave patterns exist in this system [24]. Here we use quantitative information about the kinetics to characterize this interesting system.

2 Experimental

The reaction was studied in a standard UHV stainless steel chamber operated as a continuous flow reactor (pumping speed of main chamber $S = 210\ \mathrm{l\ min^{-1}}$), equipped with low-energy electron diffraction (LEED) and a differentially pumped quadrupole mass spectrometer (QMS) for rate measurements. The Rh(110) sample of approx. (0.8×0.8) cm^2 area and 0.2 cm thickness, was prepared by repeated Ar^+ ion sputtering ($E = 1$ keV, $p_{Ar} = 2 \times 10^{-5}$ mbar, and $t = 20$ min), oxidation ($p_{o_2} = 3 \times 10^{-6}$ mbar) and annealing ($T = 1200$ K, $t = 1$ min) cycles until a sharp LEED pattern was obtained. The sample was heated indirectly by a filament behind the back side of the crystal either via radiation or electron bombardment. Gases of purity 5.0 for oxygen and 2.5 for ammonia as quoted by manufacturers (Linde AG) were used. Temperature programmed experiments were carried out using a commercial Eurotherm 2000 series PID controller.

During the rate measurements, a cone of ≈ 0.2 cm opening width connected to the differentially pumped QMS was brought 0.1 cm in front of the sample. In this way, detection of reaction products coming from the back of the sample and from the filament was avoided. NO and N_2 formation were followed via $m/e = 30$ and $m/e = 28$, respectively. With this set-up also the reactive sticking coefficient (s_{reac}) of the reactants can be determined as described previously [2]. The method is based on the fact that only those particles which are reflected by the surface can enter the cone and can thus be detected by QMS. The partial pressure variations of the reactants O_2 and NH_3 were followed using intensities (I) measured under reaction conditions; s_{reac} can be calculated as follows:

$$s_{reac} = \frac{I_0 - I}{I}.$$

Here, I represents the partial pressure with reaction, and I_0 without reaction. We assume that at $T = 300$ K the reaction rate is negligible, and therefore take the intensity value at this temperature as I_0.

3 Results and Discussion

The kinetics of N_2 and NO production were measured always starting with a freshly prepared clean surface and with a well-defined structure as verified by LEED. Figure 2 shows the temperature dependence of the product rates for different partial pressure ratios of the reactants $p_{o_2} : p_{NH_3}$, keeping the total pressure fixed at 4×10^{-5} mbar. The same y-scaling was used in all plots to allow a direct comparison of the rates. The temperature was cycled with a rate of 50 K min^{-1}. The qualitative picture obtained is similar to previous observations with Pt as catalyst [1–5]. N_2 production is the preferred reaction pathway at low temperatures and a low O_2:NH_3 ratio. With increasing temperature and/or with increasing oxygen content in the reactant gas NO production becomes substantial.

Considerable hystereses were seen in the N_2 production curves [especially for (1:1) and (3:1) O_2:NH_3 reactant ratios], and, to a smaller degree, also show up in the NO rate. Hysteresis loops for the same reaction over different stepped and non-stepped Pt single crystal surfaces and polycrystalline foil were reported in Ref. [2]; the widths found in this study for N_2 have comparable magnitudes ($\approx 10^{14}$ cm^{-2} s^{-1}). It was verified that the hystereses are true hystereses and not caused by transients, by stopping the heating/cooling schedule at certain points and checking that the rate remained stationary. The rate maximum in N_2 production for a 1:1 ratio O_2:NH_3 is around 600 K. Increasing the ratio to 3:1 does not change the rate maximum of the heating branch but at higher temperatures the rate drops strongly. Consequently, on the cooling branch the N_2 rate remains quite low. In large excess of O_2 with a ratio O_2:NH_3 of 10:1 the N_2 production is strongly suppressed and with it the NO formation. That is, the overall activity is reduced in a large excess of oxygen.

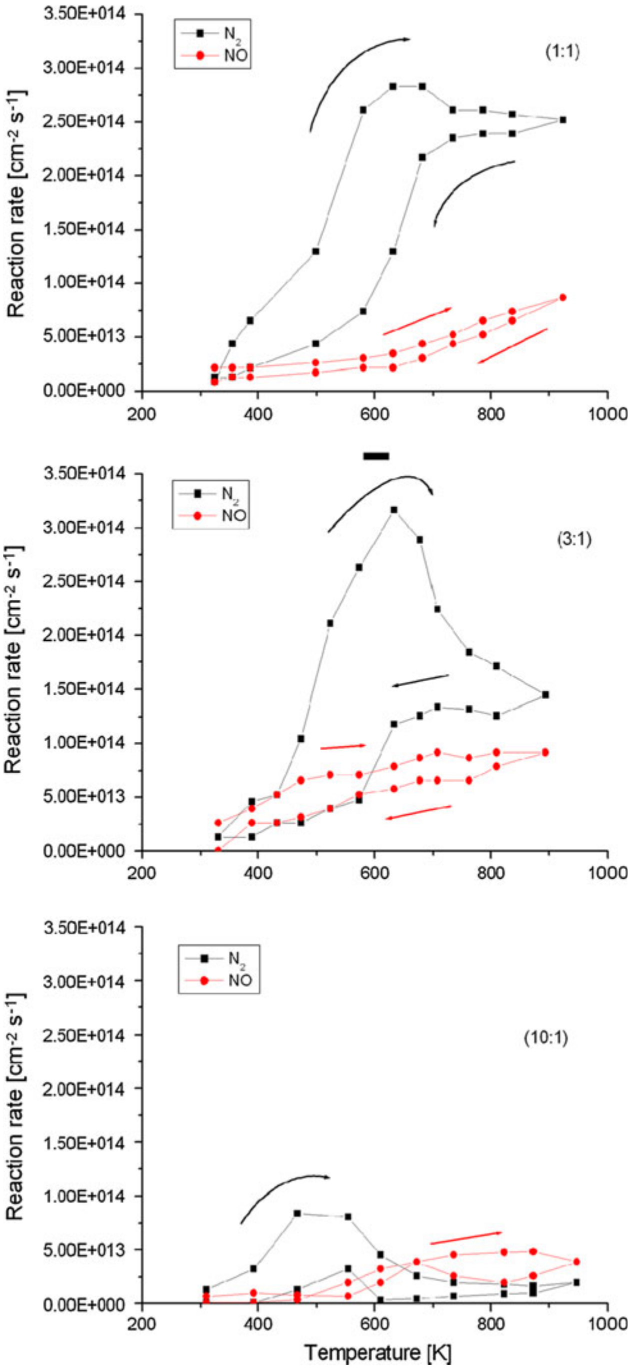

Fig. 2 Temperature dependence of the N_2 and NO production rates on Rh(110) for different ratios $p_{o_2} : p_{NH_3}$ (*upper panel*) (1:1), (*middle panel*) (3:1), and (*lower panel*) (10:1). The total pressure is 4×10^{-5} mbar in every case. *Arrows* indicate heating/cooling ($\beta = 50$ K min^{-1}). *Error bars* are indicated by the size of the symbols used to represent data points. *Solid bar* on top of middle panel for (3:1) ratio indicates the temperature range where oscillations were observed

In the pressure range from 10^{-5} to 10^{-4} mbar in which the reaction was studied, the rate scales with the total pressure, independently of the ratio of the reactants used, as demonstrated by Fig. 3. The variation of the reactive sticking coefficient of oxygen during the temperature cycling experiments of Fig. 2 is displayed in Fig. 4. In principle, s_{reac} should reflect the sum of the rates of the two product channels N_2 and NO and this is roughly the case. The maximum is observed around 0.05 which is about 5% of the initial oxygen sticking coefficient. For Rh(110)/O_2 $s_0 = 0.95$ has been reported for T = 573 K [25]. The strong reduction of sticking indicates substantial adsorbate coverage during the cycling experiments.

In analogy to ammonia oxidation on Pt, one can expect that the hystereses in the reaction rates are due to structural transformations of the surface [3, 26]. However, correlation between hysteresis loop widths and structural transformations on substrates are far from trivial, e.g., oxygen (1 × 2) islands present during surface reconstruction for the $N_2O + CO$ reaction on Pd(110) were found to cause a narrowing (and even a disappearance) of such loops in the reaction rates when a given system parameter is cycled [27].

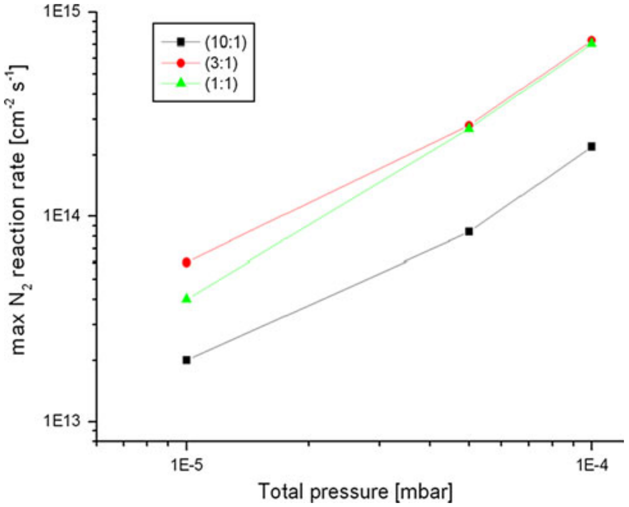

Fig. 3 Effect of total pressure on the maximum N_2 production rate for three different ratios $p_{o_2} : p_{NH_3}$: (1:1), (3:1), and (10:1)

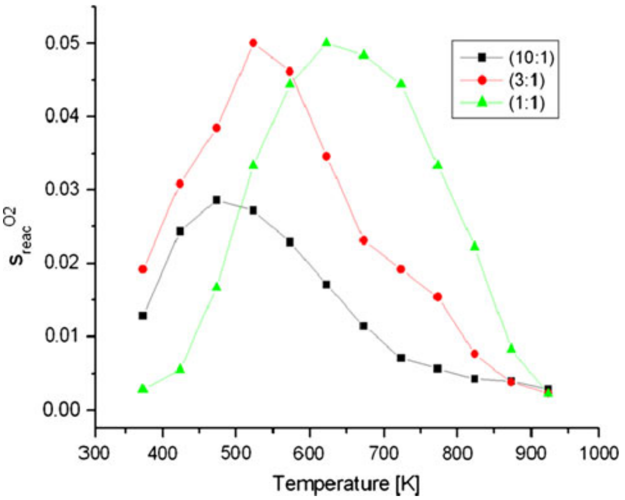

Fig. 4 Temperature dependence of the reactive sticking coefficient of O_2 for different ratios $p_{o_2} : p_{NH_3}$: (1:1), (3:1), and (10:1). The total pressure is 4×10^{-5} mbar in all cases (heating ramp $\beta = 50$ K min^{-1})

Keeping in mind previous modeling on a similar Rh(110) reaction system [21] and the facts discussed above, one can speculate on the following simplified reaction mechanism (where * denotes vacant adsorption sites, and a and g subscripts stand for adsorbed and gas phase species, respectively):

(R1) $NH_{3,g} + * \leftrightarrow NH_{3,a}$
(R2) $O_{2,g} + 2* \leftrightarrow 2O_a$
(R3) $NH_{3,a} + O_a \rightarrow NH_{2,a} + OH_a$
(R4) $NH_{2,a} + O_a \rightarrow NH_a + OH_a$
(R5) $NH_a + O_a \rightarrow N_a + OH_a$
(R6) $N_a + N_a \rightarrow N_{2,g} + 2*$
(R7) $N_a + O_a \leftrightarrow NO_a + *$
(R8) $NO_a \rightarrow NO_g + *$
(R9) $OH_a + H_a \leftrightarrow H_2O_g + 2*$
(R10) $OH_a \leftrightarrow O_a + H_a$

As was demonstrated by STM and LEED, a whole zoo of different N,O-induced reconstructions exists on Rh(110) [21]. Oxygen causes various reconstructions of the missing row type; a c(2 × 6)-O, corresponding to $\theta_o \approx 0.66$ has been identified here. With nitrogen, the added row reconstruction phases (2 × 1)-N/(3 × 1)-N may form corresponding to $\theta_N = 0.5$ and 0.33, respectively [20, 30]. In addition, a mixed co-adsorbate phase c(2 × 4)-2O,N has been reported [31]. At 10^{-6} and 10^{-5} mbar no direct evidence for the participation of these phases by in situ LEED is available but indirect evidence is provided by photoemission electron microscopy (PEEM). Different intensity levels reflecting the work function of the surface indicate that the rate hysteresis is associated with a change from a nitrogen to an oxygen covered surface [21]. The reactive state of the surface is connected with the nitrogen covered surface, and the less active branch with the oxygen covered surface. Description of the system behavior as the temperature raises can be summarized as follows: the initial state is an essentially nitrogen covered surface, caused by the reaction steps R1 and R3–R5. It was demonstrated for Pt and Rh [20, 21, 26] that moderate oxygen coverages have an accelerating effect on ammonia H-ripping reactions, and, moreover, abstraction of the first hydrogen (reaction step R3) has the highest activation barrier of the overall process leading to N ad-species. Upon heating, the N_2 production (R6 step) will be high but, as the surface is finally depleted of nitrogen due to rapid thermal N_2 desorption, the situation will change from a nitrogen covered to a mixed nitrogen/oxygen adlayer [c(2 × 4)-2O,N phase] first, and ultimately to an oxygen covered state [c(2 × 6)-O adlayer]. This reduces the catalytic activity and shifts the selectivity towards NO formation (R7–R8 steps); consequently, on the cooling branch the reaction remains on the low rate branch. The oxygen coverage determines whether reaction step R7 proceeds forwards or backwards, i.e., higher O-coverages favor NO coverages to build up and shift the selectivity towards NO production (step R8), while low values cause the N-coverage to remain high and therefore the N_2 production to be the preferred reaction pathway. Surprisingly, the transition from a nitrogen to an oxygen covered surface does not cause the NO production rate to rise strongly, the cooling branch displays lower catalytic activity. Apparently, it is the overall catalytic activity which decreases by the change in the adsorbate coverage and by the different type of surface reconstruction. Numerical simulations of a suitable reaction mechanism taking this into account are subject of future study.

A striking feature during the above described experiments was that, when the heating schedule was stopped, sustained oscillations in the reaction products N_2, NO, and H_2O developed under certain conditions, as shown in Fig. 5. At a total pressure $p \approx 4 \times 10^{-5}$ mbar, rate oscillations were observed in a temperature range 590–620 K under oxygen-rich conditions, with O_2:NH_3 ratios ranging from (4:1) to (2:1). The obtained temperature window for oscillatory behavior is comparable to previously reported values for similar reaction systems [28]. Oscillations were found to be highly sensitive to the total pressure, as higher values lead to shrinkage of the T-window and eventually to a disappearance, as the limit $p \approx 1 \times 10^{-4}$ mbar is reached. As shown in Fig. 5, the oscillations are not completely regular; one can distinguish a period $t \approx 13$ s, as marked in the plot inset.

Remarkably, the oscillations in the rate of all three reaction products were observed to be synchronized. When two possible reaction pathways are present, it is interesting

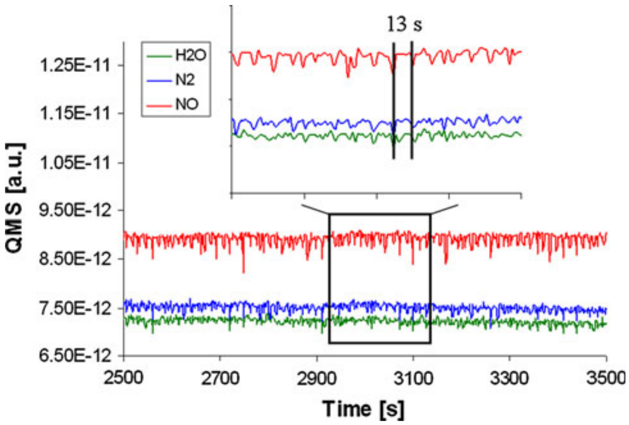

Fig. 5 Oscillations in product formation rates as measured via QMS for T = 620 K, a total pressure 4 × 10^{-5} mbar and a reactants ratio O_2:NH_3 of (4:1). *Inset* shows an enlarged section of time evolution (≈200 s.)

to establish whether in- or out-of-phase variations in the corresponding products occur or not. Siera et al. [29] recorded out-of-phase oscillations for N_2O and N_2–NH_3 production in the NO + H_2 over Pt(100) reaction system. The authors hypothesized on the availability of vacant sites at different steps of the mechanism to explain such feature, i.e., $N_2O_{(ads)}$ desorbs when free sites are not available, while it predominantly decomposes if the opposite is true, producing $N_{2(g)}$ and $O_{(ads)}$ and favoring the N_2–NH_3 reaction pathway.

Synchronized N_2 and NO product rates were obtained in the present study, allows us to speculate on a regime in which transitions between (2 × 1)/(3 × 1)-N (active) and c(2 × 4)-2O,N/c(2 × 6)-O (inactive) reconstructed phases occur, causing the observed behavior. This is, in case of high catalytic activity, removal of $N_{(ads)}$ provokes building up of an O-coverage which turns the surface inactive; ammonia adsorption and dissociation (steps R1, R3–R5) are favored then, while lifting of the active reconstructed surface reestablishes the high catalytic activity.

4 Conclusions and Outlook

We have characterized the Rh(110) surface as a very efficient catalyst in the ammonia oxidation with O_2 via a comparatively high reactive sticking coefficient reaching ≈0.05. The reaction leads predominantly to N_2 as product; a second pathway is NO formation whose contribution increases with rising temperature and a rising O_2:NH_3 ratio. Adsorbed oxygen deactivates the surface to a certain degree and accordingly the overall catalytic activity decreases with a rising O_2:NH_3 ratio. The stationary reaction rates exhibit hysteresis effects in T-cycling experiments, presumably caused by structural transformations which accompany the change from a nitrogen- to an oxygen-covered surface. At total pressures <10^{-4} mbar and temperatures ranging from 590 to 620 K, oscillations occur under oxygen rich reactant ratios. Further studies with in situ methods characterizing the chemical species and the surface structures are required in order clarify the mechanism driving the rate oscillations.

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