KINETICS OF LOW PRESSURE AMMONIA OXIDATION OVER RH(111)

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Abstract— The kinetics of the $NH_3 + O_2$ reaction over a Rh(111) single crystal catalytic surface was explored in the 10^{-6} mbar pressure range at temperatures between 300-900 K. Selectivity towards N_2 and NO products, and reactive sticking coefficients were monitored *in situ* using differentially pumped quadrupole mass spectroscopy (QMS).

Keywords— Ammonia oxidation, Photoelectron Emission Microscopy (PEEM), Oxygen reactive sticking coefficient, Ultra high vacuum techniques.

I. INTRODUCTION

Ammonia oxidation over rhodium catalysts is an important reaction in environmental catalysis and the same reaction also plays a role in industrial catalysis (Lox and Engler, 1997). In NO production via the so-called Ostwald process a Pt/Rh gauze is used containing up to 10% Rh (Chilton, 1960). In addition, ammonia oxidation over Rh was also shown to exhibit interesting nonlinear behavior (Imbihl and Ertl, 1995; Rafti *et al.*, 2012b; Rafti *et al.*, 2007; Rafti *et al.*, 2012a; Rafti *et al.*, 2015). Rate oscillations, a history dependent anisotropy of front propagation and traveling interface modulations have been observed on Rh(110) (Rafti *et al.*, 2012a; Rafti *et al.*, 2015). With scanning tunneling microscopy structural intermediates in the titration of an oxygen covered Rh(110) surface with ammonia were characterized (Kiskinova *et al.*, 1995). The adsorption of O_2; H_2; N_2; CO and NO has been the subject of numerous experimental and several theoretical investigations (Mavrikakis *et al.*, 2002). The kinetics of ammonia decomposition were investigated on various low-index single crystal planes of Rh and other catalytic surfaces (Wagner and Schmidt, 1995; Löffler and Schmidt, 1976a; Löffler and Schmidt, 1976b; Yang *et al.*, 2014). The majority of the kinetic and mechanistic studies focus on ammonia oxidation over Pt surfaces because Pt based catalysts are used in the Ostwald process (Bradley *et al.*, 1997; Bradley *et al.*, 1995; Offermans *et al.*, 2007; Offermans *et al.*, 2006; Kraehnert and Baerns, 2008). High temperature ammonia oxidation over a Rh wire was studied by Pérez-Ramirez with the TAP (temporal analysis of products) technique (Pérez-Ramirez and Kondratenko, 2007). Here we study the kinetics of ammonia oxidation over a Rh(111) surface. The main qualitative features of ammonia oxidation over Rh(111) are identical to ammonia oxidation over Pt surfaces but in details such as the sensitivity of the system to the oxygen content the $NH_3 + O_2$ reaction on Rh(111) exhibits some remarkable peculiarities (Bradley *et al.*, 1995; Offermans *et al.*, 2006).

II. METHODS

The experiments are conducted in a standard UHV system equipped with LEED (low-energy electron diffraction), an Auger electron spectrometer (AES), a photoemission electron microscope (PEEM) and a differentially pumped quadrupole mass spectrometer (QMS) for rate measurements. The Rh(111) sample was prepared by repeated Ar^+ ion sputtering (E=1keV, p_{Ar} =2×10^{-5} mbar, and t = 20 min), oxidation (p_{O2} = 3×10^{-6} mbar) and annealing (T= 1200 K, t=1 min) cycles until a sharp LEED pattern was obtained and AES showed no impurities. The sample was heated either directly through two Ta wires attached to the sides of the crystal or indirectly by electron bombardment from a filament behind the backside of the crystal. Gases of purity 5.0 for oxygen and 2.5 for ammonia (both *Linde* AG) were used after QMS check for impurities (data was not corrected for differential ionization probabilities).

During the rate measurements the sample is brought to distance of about 1 mm in front of a cone of ≈6 mm opening, which shields the differentially pumped QMS. In this way, only reaction products coming directly from the sample are detected. NO and N_2 formation were followed via *m/e* = 30 and *m/e* = 28 QMS signals respectively. PEEM was used to monitor surface work function under reaction conditions.

III. RESULTS

A. Selectivity changes due to reactants partial pressure ratio

Ammonia reacts with oxygen on Pt and Rh surfaces to give as main products N_2, NO and H_2O, via two different reaction pathways which give raise to the following global chemical equations (Bradley *et al.*, 1995; Bradley *et al.*, 1997; Offermans *et al.*, 2007),

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O, \qquad (1)$$
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O. \qquad (2)$$
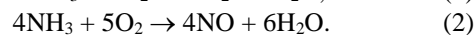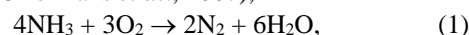
At elevated pressures ($p > 10^{-2}$ mbar) a minor amount of N_2O is also formed on Pt surfaces (Imbihl *et al.*, 2007). In the experiments conducted here, no N_2O

is detected. Figure 1 displays the temperature dependence of N_2 and NO formation for varying oxygen content of the gas atmosphere characterized by the ratio *rat* $= p(O_2)/p(NH_3)$. The experiments are conducted such that the ammonia partial pressure is kept fixed at $p(NH_3) = 5 \times 10^{-6}$ mbar while $p(O_2)$ is varied. The temperature is cycled with a heating/cooling rate of 0:5 K/s. A small hysteresis between the rates on the heating and cooling branch is found but since the hysteresis disappears if the heating/ cooling is carried out at sufficiently slow speeds, it is concluded that the hysteresis are due to transient effects. For this reason only the rates of the cooling branch are displayed. For oxygen adsorption on the clean Rh(111) surface, an initial sticking coefficient of 0:2 was reported, which agrees with this maximum value (Thiel *et al.*, 1979).

As on Pt surfaces, N_2 production is the dominant reaction channel at low temperature but with rising temperature NO formation becomes dominant (Bradley *et al.*, 1995; Offermans *et al.*, 2007). With increasing oxygen content the rate maxima of both, of N_2 and of NO production shift to lower temperature as demonstrated by Fig. 1, where the shift of the rate maxima are shown for both products. In N_2 production, the rate maximum moves from $\approx$ 670 K at *rat* = 0:04 to $\approx$ 470 K at *rat* = 5 (see Fig. 1). For NO formation one observes a similar dependence as shown in Fig. 1. For ammonia being in excess, the shift becomes quite small. The rate traces in Fig. 1 also demonstrate that the N_2 peak considerably sharpens with increasing oxygen content. With both, the N_2 and the NO traces one observes that the transition to an unreactive state at low temperature becomes much steeper with rising oxygen content.

B. Reactive sticking coefficient measurements.

With the sample brought in front of a differentially pumped cone connecting the QMS, one can measure directly the sticking coefficient of the reactants. This is possible because only those molecules reflected from the sample surface (i.e., those molecules not reacting) can enter the cone to be detected by the differentially pumped QMS. In such way, one obtains the reactive sticking coefficient (s_{reac}), of gases from the following expression:

$$s_{reac} = \frac{I_0 - I}{I}, \tag{3}$$

where I_0 refers to the QMS intensity measured for the limiting case of complete reflection; i.e., unreactive surface, and I is the intensity measured for the reacting catalytic surface. The reactive sticking coefficient of oxygen, $s_{reac}(O_2)$, is displayed in Fig. 2 for two different O_2/NH_3 ratios, *rat* = 0.04 and *rat* = 0.2. The reactive sticking coefficient according to Eq. (1) and Eq. (2) representing the sum of the two reaction channels, $r(N_2)$ + $r(NO)$, rises from 400 K to 650 K. After passing through a shallow maximum $s_{reac}(O_2)$ reaches an almost plateau-like high level for *rat* = 0:04.

With ammonia being strongly in excess, $s_{reac}(O_2)$ reaches a maximum value of $\approx$ 0:25. Increasing the ox-
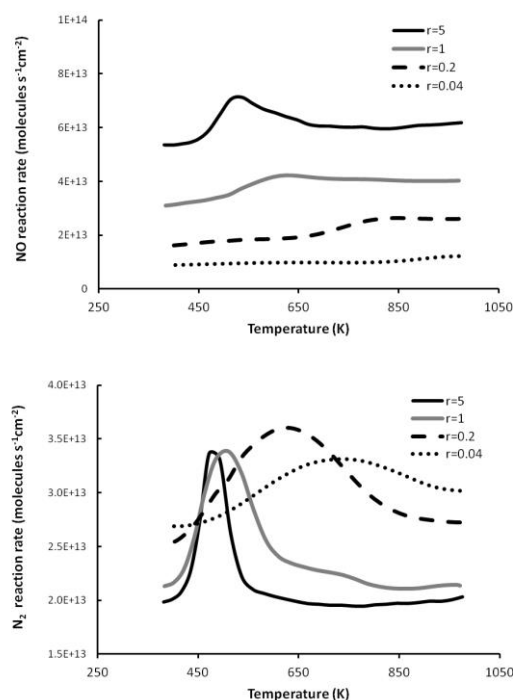

Figure 1: Temperature dependence of the NO (top panel) and N_2 (bottom panel) production rates on Rh(111) for different ratios *rat* $= p(O_2)/p(NH_3)$, while keeping fixed $p(NH_3) = 5 \times 10^{-6}$ mbar.

ygen content on the reactants mixture by a factor of five reduces the maximum of $s_{reac}(O_2)$ by 60% to only 0.1. Evidently, as demonstrated by the plateau-like high value of $s_{reac}(O_2)$ beyond 600 K, there is hardly any inhibition of oxygen adsorption by $NH_x(x = 0-3)$ fragments. PEEM images included in Fig. 2 for *rat* = 0.2, display a uniform dark surface for this range, suggesting that the surface is oxygen covered. So it is apparently the oxygen coverage which limits the adsorption of oxygen in this range. One can check the consistency of the rate measurements and of $s_{reac}(O_2)$ because under steady state conditions the amount of oxygen adsorbing per second has to be equal the sum of H_2O and NO production; i.e., equal to $2 \times r_{ad}(O_2) = r(H_2O) + r(NO)$. Conversely, the amount of nitrogen in ammonia adsorbing per second has to be equal the production rates of N_2 and NO according to $r_{ad}(NH_3) = 2 \times r(N_2) + r(NO)$. Within 10-20% this balance is fulfilled in the range from 350 - 950 K.

The spatiotemporal behavior of the $NH_3 + O_2$ reaction on Rh(111) was monitored in the 10^{-6} mbar range with PEEM, but neither reaction fronts nor any other wave patterns were detected. The changes in the surface coverages all take place in a spatially homogeneous way. That is, one observes a spatially uniform darkening or brightening of the surface upon a parameter change. This behavior is quite different from the $NH_3 + O_2$ reaction on Rh(110) where bistability and reaction fronts were observed (Rafti *et al.*, 2015).
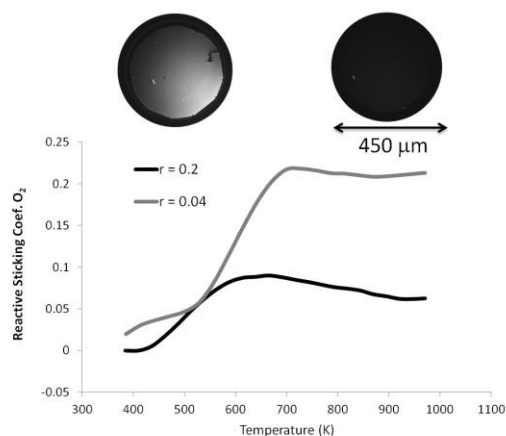
Figure 2: Temperature dependence of the oxygen reactive sticking coefficient on Rh(111) for different ratios $rat=p(O_2)/p(NH_3)$, while keeping fixed $p(NH_3) = 5 \times 10^{-6}$ mbar. PEEM images corresponding to the states of the surface for $rat = 0.2$ at low and high temperatures are depicted on the top panels.

III. CONCLUSIONS

We have studied the ammonia oxidation reaction with oxygen in the 1×10^{-6} mbar pressure regime using both local and global methods in order to gain further insight into the mechanism and to check for possible non-linear dynamics. From QMS measurements, we have established that both selectivity and reactivity strongly depend on reactants ratio used and catalyst temperature. Similar to what was observed for other Pt and Rh single crystal catalysts, increasing temperature and oxygen proportion values favors the production of NO in detriment of N_2, while temperature range for the formation of both products sharpens as oxygen ratio is increased in the reactants mixture. We have also demonstrated via reactive sticking coefficient measurements for different reactants ratio, that a decrease in $s_{reac}(O_2)$ consistent with an *autoblocking* effect takes place. This is, an increment of oxygen ratio in the reactant mixture, causes the surface to become increasingly occupied as temperature raises, and thus reactive sticking coefficient decrease. Different from ammonia oxidation reaction over Rh(110) single crystal catalysts, where non-linear dynamics giving rise to reaction fronts and phase transitions were observed, Rh(111) surface lacks of any non-linear behavior as temperature and partial pressures of reactants is varied. Instead homogeneous brightness changes are observed in PEEM experiments. As the temperature and/or oxygen partial pressure are increased, the surface changes from a state of high $NH_x(x = 0 - 3)$ coverage and low work function to an oxygen covered state of high work function. The comparison of Rh(111) with Rh(110) demonstrates the crucial role of adsorbate-induced surface phase transitions for generating non-linear phenomena like rate oscillations and chemical waves.

REFERENCES

Bradley, J.M., A. Hopkinson and D.A. King, "Control of a Biphasic Surface Reaction by Oxygen Coverage: The Catalytic Oxidation of Ammonia over Pt{100}," *J. Phys. Chem.*, **99**, 17032-17042 (1995).

Bradley, J.M., A. Hopkinson and D.A. King, "A molecular beam study of ammonia adsorption on Pt{100}," *Surf. Sci.*, **371**, 255-263 (1997).

Chilton, T.H., *The manufacture of nitric acid by the oxidation of ammonia*, Chemical Engineering Progress Monograph Series, American Institute of Chemical Engineers, New York (1960).

Imbihl, R. and G. Ertl, "Oscillatory kinetics in heterogeneous catalysis," *Chem. Rev.*, **95**, 697-733 (1995).

Imbihl, R., A. Scheibe, Y.F. Zeng, S. Günther, R. Kraehnert, V.A. Kondratenko, M. Baerns, W.K. Offermans, A.P.J. Jansen and R.A. van Santen, "Catalytic ammonia oxidation on platinum: mechanism and catalyst restructuring at high and low pressure," *Phys. Chem. Chem. Phys.*, **9**, 3522-3540 (2007).

Kiskinova, M., A. Baraldi, R. Rosei, R. Dhanak, G. Thornton, F. Liebsle and M. Bowker, "Surface structural transformations during ammonia oxidation on Rh(110)," *Phys. Rev. B*, **52**, 1532-1535 (1995).

Kraehnert, R. and M. Baerns, "Kinetics of ammonia oxidation over Pt foil studied in a micro-structured quartz-reactor," *Chem. Eng. J.*, **137**, 361-375 (2008).

Löffler, D.G. and L.D. Schmidt, "Kinetics of NH_3 decomposition on single crystal planes of Pt," *Surf. Sci.*, **59**, 195-204 (1976a).

Löffler, D.G. and L.D. Schmidt, "Kinetics of NH_3 decomposition on Polycristalline Pt," *J. Catal.*, **41**, 440-454 (1976b).

Lox, E.S.J. and B.H. Engler, "Environmental catalysis," *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knzinger and J. Weitkamp (eds.), VCH Weinheim, **4**, 1581 (1997).

Mavrikakis, M., J. Rempel, J. Greeley, J., L.B. Hansen and J.K. Norskov, "Atomic and molecular adsorption on Rh(111)," *J. Chem. Phys.*, **117**, 6737-6744 (2002).

Offermans, W.K., A.P.J. Jansen and R.A. van Santen, "Ammonia activation on platinum {1 1 1}: A density functional theory study," *Surf. Sci.*, **600**, 1714-1734 (2006).

Offermans, W.K., A.P.J. Jansen, R.A. van Santen, G. Novell-Leruth, J.M. Ricart and J. Pérez-Ramírez, "Ammonia Dissociation on Pt{100}, Pt{111}, and Pt{211}: A Comparative Density Functional Theory Study," *J. Phys. Chem. C*, **111**, 17551-17557 (2007).

Pérez-Ramirez, J. and E.V. Kondratenko, "Evolution, achievements, and perspectives of the TAP technique," *Catal. Today*, **121**, 160-169 (2007).

Rafti, M., F. Lovis, Y.F. Zeng and R. Imbihl, "Homogeneous and front-induced surface transformations during catalytic oxidation of ammonia over Pt (100)," *Chem. Phys. Lett.*, **446**, 323-328 (2007).

Rafti, M., F. Lovis and R. Imbihl, "The O_2 + NH_3 Reaction Over Rh(110): Steady State Kinetics and Oscillatory Behavior," *Catal. Lett.*, **142**, 16-21 (2012a).

Rafti, M., H. Uecker, F. Lovis, V. Krupennikova and R. Imbihl, "Traveling interface modulations in the NH 3+ O 2 reaction on a Rh (110) surface," *Phys. Chem. Chem. Phys.*, **14**, 5260-5264 (2012b).

Rafti, M., B. Borkenhagen, G. Lilienkamp, F. Lovis, T. Smolinsky and R. Imbihl, "Traveling interface modulations and anisotropic front propagation in ammonia oxidation over Rh(110)," *J. Chem. Phys.*, **143**, 184701 (2015).

Thiel, P.A., J.T. Yates, and W.H. Weinberg, "The interaction of oxygen with the Rh(111) surface," *Surf. Sci.*, **82**, 22-44 (1979).

Wagner, M.L. and L.D. Schmidt, "Model Catalytic Oxidation Reactions: Oxygen with H_2, NH_3, and N_2H_4 on Rh(111)," *J. Phys. Chem.*, **99**, 805-815 (1995).

Yang, S., S. Xiong, Y. Liao, X. Xiao, F. Qi, Y. Peng, Y. Fu, W. Shan and J. Li, "Mechanism of N_2O formation during the low-temperature selective catalytic reduction of NO with NH_3 over Mn–Fe spinel," *Environ. Sci. Technol.*, **48**, 10354-10362 (2014).