



## ***In situ* X-ray photoelectron spectroscopy of ammonia oxidation on Pt(533)**

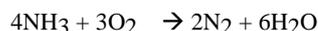
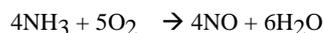
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### **Introduction**

We have used *in situ* X-ray photoelectron spectroscopy (XPS) to investigate the catalytic oxidation of ammonia with oxygen on a Pt(533) surface. The high temperature oxidation of ammonia with oxygen to NO on platinum in the so-called Ostwaldt process is one of the most important industrial chemical reactions. At low temperature ( $T < 800$  K) mainly  $N_2$  and to a smaller degree also  $N_2O$  are obtained:



In a LEED/STM study it was shown that the Pt(533) surface (4(111)x(100) in Somorjai notation) undergoes restructuring under reaction conditions leading to a doubling of the step height of the (100) steps and to a doubling of the width of the (111) terrace units [1]. The restructuring was associated with a change in selectivity from preferential  $N_2$  on the original surface to dominant NO production on the restructured surface. Our goal was to identify the reacting surface species over a broad pressure range and to determine whether the prevailing species change as a consequence of the pressure change and as a consequence of reaction-induced surface restructuring.

### **Experimental**

The maximum pressure used during the experiments was  $\sim 1$  mbar. X-rays are admitted to the experimental cell through a 100 nm thick  $SiN_x$  window. The photoelectrons emitted from the sample or the gas phase enter a differentially pumped electrostatic lens system through a 1 mm diameter aperture. They pass two additional apertures before being focused into the focal plane of a standard elec-

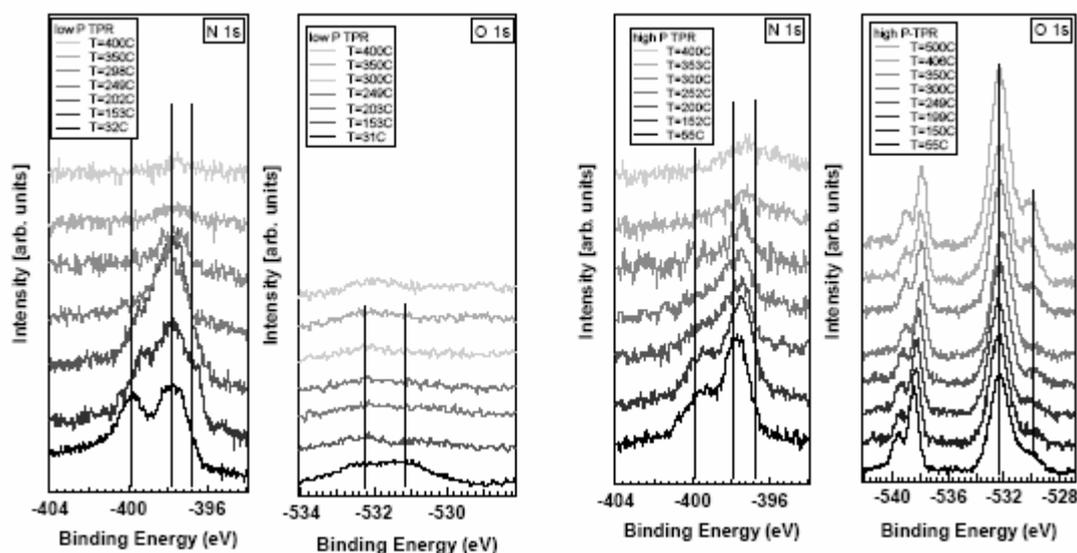
tron energy analyzer. The N 1s and the O 1s spectra shown in this report were obtained by using photons of 690 and 830 eV, respectively. The experiments were performed at the undulator beam line U49/2-PGM1.

### **Results**

During adsorption of  $NH_3$  at least three different components in the N 1s spectra were detectable. These species are present on the Pt(533) in the low temperature regime ( $T < 250$  C) of ammonia oxidation in the  $10^{-4}$  and  $10^{-1}$  mbar range.

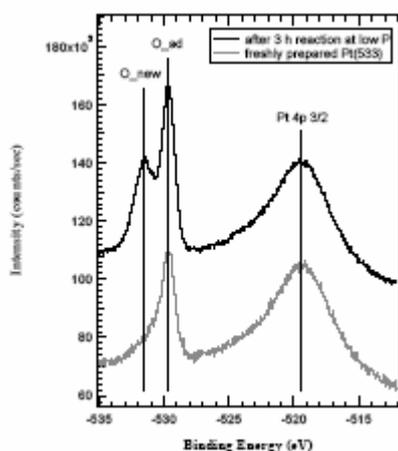
Figure 1 shows the N 1s and O 1s spectra obtained from the Pt(533) sample (and the gas phase) *in situ* during the reaction. Clearly the N 1s species present on the sample during the reaction are very similar in the two pressure ranges. The oxygen species present on Pt(533) in the low and in the high pressure experiment vary substantially. The main reason for this difference is that the surface is partially contaminated by carbon during the reaction in the low pressure regime. As a consequence oxygen is immediately reacted off from the surface.

Besides the O 1s peak obtained from molecular oxygen of the gas phase (between 538 and 540 eV) several adsorbed oxygen species are well visible in Fig. 1. At high pressure a new oxygen species at 532.2 eV is visible beside the known species at 529.7 eV of atomic adsorbed oxygen. Note that atomic oxygen is present on the surface at low temperature, then nearly no intensity is found in an intermediate temperature interval from 200 °C to 300 °C and a substantial amount of oxygen is again present at high temperatures above 350 C. This T-dependent behavior of the oxygen coverage as well as the of nitrogen containing adsorbates could be reproduced in a realistic mathematical model simulating ammonia oxidation with mean field differential equations. One key input for the model is the fact that adsorbed NO already decomposes on Pt(533) above 70 °C.



**Figure 1:** In situ O 1s and N 1s spectra obtained during the catalytic ammonia oxidation at various temperatures. Low pressure experiment  $P(\text{O}_2) = 3 \times 10^{-4}$  and  $P(\text{NH}_3) = 1 \times 10^{-4}$  mbar, high pressure experiment  $P(\text{O}_2) = 5.75 \times 10^{-1}$  and  $P(\text{NH}_3) = 0.65 \times 10^{-1}$  mbar

The new oxygen component at 532.2 eV accumulated during the  $\text{NH}_3 + \text{O}_2$  reaction in the high pressure experiment turned out to be highly stable because it could not be removed by  $\text{NH}_3$  reduction at 500 °C and 1 mbar. This species is also built up during low pressure reaction conditions but only to a modest amount when repeating several temperature programmed reaction cycles.



**Figure 2:** O 1s and Pt  $4p_{3/2}$  spectra of a freshly prepared Pt(533)-surface and the surface after 3 hours reaction in ammonia and oxygen.

Fig. 2 shows the O 1s spectrum from a freshly prepared Pt(533) surface and a surface which has been temperature cycled (3 ramps from 30 °C to 550 °C and back) in  $p(\text{O}_2) = 1 \times 10^{-3}$  and  $p(\text{NH}_3) = 1 \times 10^{-4}$  mbar for 3 hours. The accumulation of oxygen is clearly visible. The total oxygen coverage of this particular experiment is still below one monolayer assuming a saturation coverage of 0.25 ML for adsorbed oxygen on Pt(111). Although it is known that high oxygen coverages on Pt(111) are possible if other O-sources than  $\text{O}_2$  adsorption are applied [2], to our knowledge the observed component is not reported in the literature. It should be noted that this species developed exclusively during the ammonia oxidation experiments. The identification of the new oxygen species at 532.2 eV and the clarification whether this species is a signature of the pressure gap will be the aim of future experiments.

## Acknowledgements

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## References

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- [2] N. A. Saliba, Y. L. Tsai, C. Panja, B. E. Koel, Surf. Sci. **419** (1999) 79-88.