

A kinetic and *in-situ* XPS study of the NO oxidation reaction on a Pt(111) single crystal

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Introduction

The NO oxidation reaction ($\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2$) on platinum is the first step in the NO_x storage and reduction process (NSR) being developed for diesel engines. In previous studies, the turnover rate (TOR) was shown to be a strong function of platinum particle size with higher rates occurring on larger particles implying that the reaction is structure sensitive. To better understand this effect, a kinetic study was performed on a Pt(111) single crystal at the same conditions used on supported catalysts. The surface coverage of oxygen and nitrogen species as well as the oxidation state of Pt under simulated reaction conditions was studied by *in-situ* X-Ray Photoelectron Spectroscopy (XPS).

Materials and Methods

The kinetic study was performed in a custom atmospheric pressure batch reactor system combined with an ultrahigh vacuum (UHV) system which allows for *in-vacuum* sample transfer. A gas phase FTIR spectrometer was used to measure NO and NO₂ concentrations in the batch reactor. The Pt(111) was heated by passing electrical current through it. A K-type thermocouple was spot welded to the side of the crystal for temperature measurement. The UHV chamber contains a sputter gun for sample cleaning, mass spectrometer, low energy electron diffraction (LEED), and a cylindrical mirror analyzer (CMA) with electron gun for Auger electron spectroscopy (AES). The sample was cleaned by repeated argon sputtering and annealing to 800°C and verified using AES. The Pt crystal structure was verified by LEED after annealing. AES was also used for post reaction analysis. The Pt TOR was determined using simple numerical methods in order to account for the homogenous gas-phase reaction as well as approach to equilibrium.

In-situ X-Ray Photoelectron Spectroscopy (XPS) experiments were performed at the Ambient Pressure Photoemission Endstation, Beamline 9.3.2, at the Advanced Light Source (ALS), Lawrence Berkeley National Labs (LBNL). The endstation consists of a sample preparation chamber which has a sputter gun for sample cleaning and an analytical chamber which allows pressures up to a few Torr in the analysis chamber during XP spectra acquisition. Oxygen coverage was calibrated using two well known conditions in the surface science literature.

Results and Discussion

Preliminary results from the kinetic study on the Pt(111) single crystal shows the highest activity reported in literature. For example, at 250°C, 159ppm NO, 40ppm NO₂, 10% O₂ and N₂ balance, the TOR is $0.23 \pm 0.05 \text{ s}^{-1}$, approximately 260 times greater than a Pt/Al₂O₃ monolithic catalyst with an average particle size of 2.3 nm reported by Mulla *et al.* [1]. The apparent activation energy (E_a) and O₂ order decreased significantly from the 2.3nm catalyst which had an E_a of 82 kJ/mol and O₂ order of 1 to $64 \pm 6 \text{ kJ/mol}$ and 0.5 ± 0.1 , but the NO and NO₂ orders remained the same at about 1 and -1 respectively. Since the Pt(111) surface

represents the dominant surface orientation of Pt under the limit of large particle size, and the rates increase with particle size, it is expected that the TOR on a Pt(111) single crystal represents the highest TOR possible on a platinum catalyst without support effects.

To determine the oxygen coverage under reaction conditions, the Pt(111) was exposed to 0.275 torr NO₂ at 250°C which yielded an atomic oxygen coverage of $0.7 \pm 0.1 \text{ ML}$. The error represents the standard deviation of five repeat measurements. No surface nitrogen species and Pt oxide formation were observed during the experiment which lasted about an hour. Since NO₂ is a much more effective oxidizer than O₂, we believe that the maximum oxygen coverage on a Pt(111) single crystal is 0.75 ML even with the addition of O₂ up to 1 bar at 250°C. Figure 1 shows an example of the XP spectra and peak deconvolution.

According to Mulla and co-workers [1], metallic Pt is the active state of Pt in the NO oxidation reaction and the Pt oxide is inactive. Based on the kinetics and *in-situ* XPS results presented here along with the work of Mulla, we believe that large platinum particles resist oxide formation due to the closed-packed structure and remain active whereas small particles which have a more open structure on average are more easily oxidized and become inactive. This hypothesis does not explain the decrease in activation energy and O₂ order and therefore a change in the reaction pathway could be occurring. Further work needs to be done to confirm these preliminary results and to better understand the changes in the E_a and O₂ order.

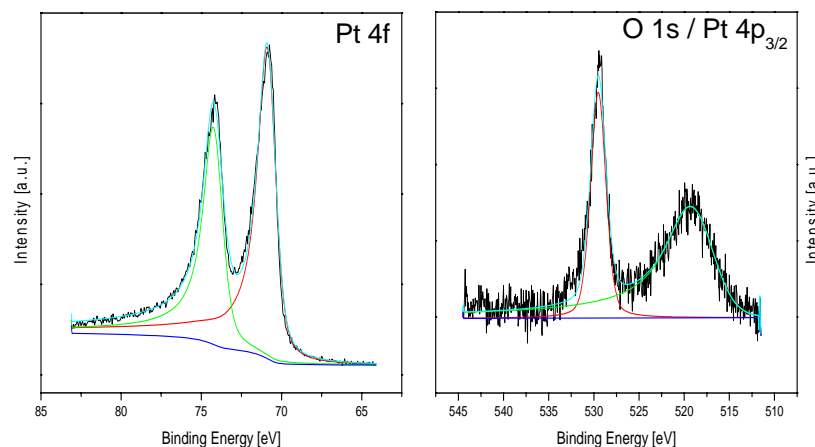


Figure 1. Pt 4f and O 1s/ Pt 4p_{3/2} spectra collected from the Pt(111) surface at 180°C in 1×10^{-7} Torr NO₂

References

1. Mulla, S.S., Chen, N., Cumarantunge L, Blau, G.E., Zemlyanov, D.Y., Delgass, W.N., Ribeiro, F.H., *J. Catal.* 241, 389 (2006)