

Understanding the Effect of Platinum Particle Size on the Rate of NO Oxidation

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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 NOx storage and reduction process (NSR), a technology currently being commercialized for emissions reduction in diesel engines. In previous studies in our group [1], the turnover rate (TOR) was shown to be a strong function of platinum particle size with higher TOR occurring on catalysts with lower dispersions indicating that this reaction may be sensitive to the structure of the Pt surface. Our studies on supported Pt suggest that the particle size effect can be attributed mainly to the oxidation of small, <3nm, particles by NO₂ as oxides of Pt are inactive for NO oxidation, however, it is not clear if an underlying structure sensitivity also exists. To further interrogate this apparent structure sensitivity, the kinetics were measured on Pt(111) which represents the dominate surface present on large, 5-10nm Pt particles and also on the Pt(321), which represents the coordinatively unsaturated surfaces found on small, <3nm particles at the same conditions used on supported catalysts. *In-situ* X-ray photoelectron spectroscopy (XPS) experiments on Pt(111) were used to verify the assumptions made in our Langmuir Hinshelwood (L-H) model by probing surface intermediates under reaction conditions.

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. Data for each condition was collected over one or two batch reactions in order to avoid complications with catalyst deactivation and accumulation of impurities from the reaction gas on the surface. The TOR on Pt was determined taking into account the homogenous gas phase reaction as well as the approach to equilibrium. The resulting data set allowed us to accurately determine apparent activation energies and reaction orders for NO, NO₂, and O₂ using a simple power rate law.

In-situ X-Ray Photoelectron Spectroscopy (XPS) experiments were performed at the Ambient Pressure Photoemission Endstation, Beamline 9.3.2.1, at the Advanced Light Source (ALS), Lawrence Berkeley National Labs (LBL). The system allows pressures up to a few Torr in the analysis chamber during XP spectra acquisition.

Results and Discussion

Results from the kinetic study on the Pt(111) and Pt(321) suggest that no significant underlying structure activity relationship exists. The TORs on the single crystals at standard conditions are the same as the highest initial rates measured on supported Pt, shown in Figure 1. Both Pt(111) and Pt(321) rates showed similar apparent activation energies and reaction orders for NO and NO₂, of 45kJ/mol, 1, and -1 respectively. In contrast, the reaction order for

O₂ on Pt(111) was close to 0.5 and 0.9 on Pt(321), which suggests Pt(111) is somewhat more efficient at adsorbing O₂ on surfaces crowded with atomic oxygen, which is the rate determining step in our L-H model. However, this difference is not significant enough to explain the order of magnitude change in the TOR with particle size found on supported Pt. *Ex situ* AES after evacuation of reaction gas and then cooling, indicates that no significant Pt oxidation occurred. The oxygen coverages on Pt(111) and Pt(321) were the same, regardless of conditions, to within experimental error, 0.66 ± 0.18 and 0.65 ± 0.12 ML respectively.

In Situ XPS was performed in order to determine the amount and chemical identity of Pt-bound oxygen under reaction conditions on Pt(111) as well as provide evidence for our proposed Langmuir-Hinshelwood (L-H) mechanism. In a series of experiments, we show that at near equilibrium conditions, the ratio of NO:NO₂ controls the coverage of oxygen on the surface, rather than the reactant O₂, and therefore the availability of empty sites for adsorption of O₂, the proposed rate determining step in our L-H mechanism. A comparison of oxygen coverage with equal chemical potentials of O₂, NO + NO₂, and all three combined is shown in Figure 2. The experiments show why the product NO₂ effectively inhibits the forward reaction rate by competing with sites with O₂.

Significance

Kinetic studies on the single crystals show that the rate of NO oxidation is independent of the structure of the platinum surface and is not responsible for the dramatic increase in TOR with increasing particle size on supported Pt. *In situ* XAS on supported Pt with varying particle size and support (not shown here) combined with kinetic and deactivation studies demonstrates that oxidation, and therefore deactivation, of small Pt particles is responsible for the apparent structure sensitivity.

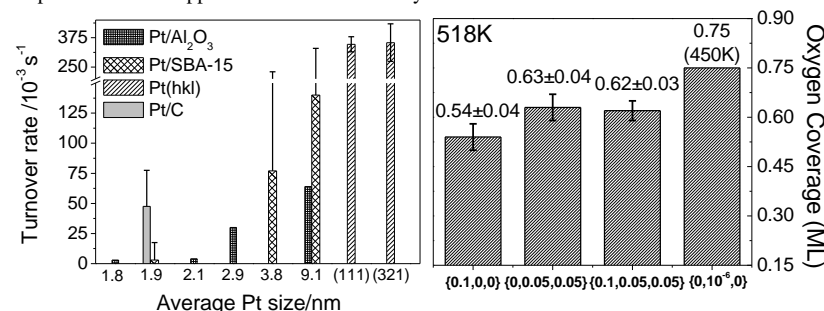


Figure 1(left). TOR at 250°C, 300ppm NO, 170ppm NO₂, and 10% O₂ for Pt catalysts with varying particle size and support in comparison TOR measured on Pt(111) and Pt(321) single crystals. One sided error bars on supported Pt data indicate the initial rates while the columns indicate the rate after stabilization. Two sided error bars on the single crystal data indicate the standard deviation of the initial rates, which are represented by the columns.

Figure 2(right). Oxygen coverage measured by *in situ* XPS under NO oxidation on Pt(111). Values in brackets indicate the pressures in Torr for O₂, NO, and NO₂ respectively. The error bars represent the standard deviation from repeat measurements of the oxygen coverage.

References

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