EXAFS Model of 2-Dimensional Platinum Clusters

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Abstract. Highly dispersed supported platinum clusters have been extensively studied because of their many uses as the active metallic component in heterogeneous catalysts, including catalytic reforming. EXAFS modelling has been used to determine the average coordination number for the first through fifth Pt shells and thereby determine the average cluster size and shape. Several studies have shown that Pt clusters on γ-Al₂O₃ are truncated to form plate-like clusters in the hexagonal (111) plane as evidenced by an overly reduced second shell coordination number, which would be zero for a truly 2-dimensional cluster. In our system of Pt on γ-Al₂O₃ the average Pt morphology is determined, on the average, to be small ~13 atom clusters that are 2-dimensional in the hexagonal (111) plane morphology as determined by first and, nearly zero, second nearest neighbour coordination numbers of 4.4 ± 0.6 and 0.5 ± 0.3, respectively.

1. Introduction
The diverse applications of the catalytic properties of supported Pt clusters have resulted in extensive studies to elucidate the relationship between Pt cluster structure and catalytic performance. Several studies have reported Pt EXAFS modelling up to the 5th shell from catalysts with Pt loading of 1-2wt% [1-3]. Munoz-Paez et al. [1] found that depending on the details of oxidation/reduction that fully reduced Pt clusters have a 1st and 2nd CN of 7.2-10.1 ± 0.3 and 2.0-2.8 ± 0.3, respectively, and characterized these clusters as spherical. In the study by Giovanetti et al. [3] the increased flatness of Pt clusters were identified by a decrease in the first nearest-neighbor (NN) coordination number (CN) and an increase in average cluster diameter determined using SAXS. In this study the first and second CN of the spherical to flattened clusters were reported to change from 9.3 ± 0.5 to 7.2 ± 0.7 and from 4 ± 1 to 4 ± 2, respectively, illustrating the clusters are quite large with significant number of layers in the <110> direction (2nd CN > 0). Cuenya et al. [2] described the EXAFS results for a ~22 atom cluster of two atomic layers prepared by the inverse micelle method. Cuenya et al. [2] showed Pt clusters can be truncated to form plate-like clusters in the hexagonal (111) plane as evidenced by an overly reduced second shell coordination number, which would be zero for a truly 2-dimensional cluster. In this paper, we describe the EXAFS modelling of 2-dimensional ~13 atom (<1nm diameter) hydrogen-saturated Pt clusters supported on γ-Al₂O₃.

2. Methods
Chloroplatinic acid was impregnated onto γ-Al₂O₃ with a surface area of 162 m²/g. The Pt loading was determined using ICP to be 0.4wt%. The catalyst was calcined at 525°C prior to the in situ XAFS experiments and then reduced in situ to a temperature of 300°C at a ramp rate of 10°C/min in flow of 100% H₂ using a custom designed XAFS cell [4]. After in situ reduction, Pt EXAFS spectra were collected at room temperature in a flow of 100% H₂ and are assumed to represent Pt clusters saturated
with hydrogen. The sample is referred to as 300°C-reduced. EXAFS spectra were collected in fluorescence mode at the MR-CAT beamline 10ID at Argonne National Laboratory.

**Table 1. EXAFS paths and parameterization**

| Path         | Description        | CN | Reff (Å) | CN | ΔR  | σ²     | EXAFS Parameterization   |
|--------------|--------------------|----|----------|----|-----|--------|--------------------------|
| Pt0-O        | Support O          | 6  | 2.5      | NO| delRO| sigO   |                         |
| Pt0-Pt1      | 1st Shell          | 12 | 2.77     | NPt1| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt2      | 2nd Shell          | 6  | 3.92     | NPt2| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt1b-Pt1a| Triangle           | 48 | 4.26     | NPt1·4| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt3      | 3rd Shell          | 24 | 4.80     | NPt3| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt1a-Pt1b| Triangle           | 48 | 5.17     | NPt1·4| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt3-Pt1  | Triangle           | 96 | 5.17     | NPt3·4| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt4      | 4th Shell          | 12 | 5.54     | NPt4| α4·Reff| Debye(Td4, Temp)        |
| Pt0-Pt4-Pt1  | Collinear MS       | 24 | 5.54     | NPt4·2| α4·Reff| Debye(Td4, Temp)        |
| Pt0-Pt1-Pt0-Pt1| Collinear MS     | 12 | 5.54     | NPt1| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt1-Pt4-Pt1| Collinear MS     | 12 | 5.54     | NPt4| α4·Reff| Debye(Td4, Temp)        |
| Pt0-Pt1-Pt3-Pt1| Triangle         | 48 | 5.54     | NPt3·2| α·Reff| Debye(Td, Temp)         |
| Pt0-Pt5      | 5th Shell          | 24 | 6.09     | NPt5| α·Reff| Debye(Td, Temp)         |

*aOne energy shift parameter for all paths was also determined.

The EXAFS spectra were modeled using FEFFIT[5] and FEFF7.0[6] for the theoretical calculations based on structure of bulk fcc Pt. The EXAFS models include single and multiple scattering paths[7,8] from Pt and also a long Pt-support O signal[9]. Each of the 5 shells of Pt atoms about the absorbing (Pt0) atom is denoted with the nomenclature of Pt1, Pt2, Pt3, Pt4 and Pt5. These paths and their parameterization are listed in Table 1. There are 13 parameters used to describe the model: 6 coordination numbers (CN), 3 change in path length (ΔR), 2 Debye Temperatures (Td), one σ², and an energy shift parameter (ΔE). The ΔR values are described in terms of an expansion/contraction term α which is a constant factor multiplied by the reference path length (Reff). The mean square displacement values (σ²) are described in terms of a Debye model with characteristic Debye temperature Td. The value for S₀² (0.93 ± 0.05) was determined from Pt foil. The data range from 3.5 to 10 Å⁻¹ was used in the Fourier transform with k-weight of 1, 2 and 3. The initial model was applied to the Fourier transformed (FT) range of 1.2 to 6 Å, containing 24 independent points and 13 parameters. Further tests were performed to determine if each of the Pt shells required independent α and Td values. Comparisons of the reduced-χ² values were made over the data range dominated by the higher shells from 3.2 to 6.0 Å containing 15 independent points and 7 parameters.

### 3. Results and Discussion

The Pt L₃-edge magnitude and real part of the EXAFS spectra are shown in Figure 1 for the 300°C-reduced and Pt foil. The EXAFS spectrum from the in situ reduced catalyst has significantly smaller amplitude compared to Pt foil. The real part of the FT shows that the signal at 2Å differs from Pt foil and the modeling confirms that it is dominated by Pt0-O from the Al₂O₃ support. The dramatic difference in the catalyst spectrum as compared to the Pt foil spectrum is a result of the nanometer-sized Pt clusters in the former.
Figure 1. Magnitude (A) and real part of Fourier transform of 300C-reduced (symbols) and Pt foil (solid).

Five test models allowed each of the 5 shells in turn to have independent $\alpha$ and Td parameters but only independent values for the 4th shell were found to have a significant difference in the ability of the model to reproduce the measured spectrum. The reduced- $\chi^2$ values are compared over the data range where the 3rd through 5th shells contribute to the data between 3.2 and 6.0 Å. The measure of the quality of the model, the reduced- $\chi^2$ for the best-fit model with unique values for the 4th Pt shell is 2 times smaller as compared to the test model with only one $\alpha$ and Td, indicating that independent 4th shell parameters are supported by the measured data. The magnitude and real part of the 300°C-reduced spectrum and the best-fit model are shown in Figure 2. The EXAFS results are listed in Table 2 for CN, $\Delta R$, and $\sigma^2$. The best-fit values for $\alpha$, $\alpha_4$, Td, and Td4 are $-0.018 \pm 0.001$, $-0.026 \pm 0.004$, and $198 \pm 13$K, and $174 \pm 55$K, respectively.

Table 1. EXAFS modelling results. Only values for single scattering paths are reported.a

| Path     | CN     | $R$ (Å) | $\sigma^2 \times 10^{-3}$ (Å²) |
|----------|--------|---------|-------------------------------|
| Pt0-O    | 1.5 ± 0.3 | 2.497 ± 0.015 | 8 ± 2 |
| Pt0-Pt1  | 4.4 ± 0.6 | 2.721 ± 0.003 | 7 ± 1 |
| Pt0-Pt2  | 0.5 ± 0.3 | 3.848 ± 0.005 | 9 ± 1 |
| Pt0-Pt3  | 1.3 ± 0.8 | 4.713 ± 0.006 | 9 ± 1 |
| Pt0-Pt4  | 1.1 ± 0.8 | 5.395 ± 0.023 | 12 ± 8 |
| Pt0-Pt5  | 1.6 ± 1.4 | 6.085 ± 0.007 | 10 ± 1 |

aEnergy shift parameter was determined to be $-0.4 \pm 0.5$ eV

The EXAFS CN can be used to determine the average cluster geometry [Frenkel 1999]. The nearly zero value for NPt2, and the very small value for NPt3 suggests that the cluster conforms to a single layer in the hexagonal Pt (111) plane. A schematic of such a cluster shown in the inset of Figure 2 and is consistent with the EXAFS determined CNs. This cluster has NPt1, NPt2, NPt3, NPt4, and NPt5 values of 3.7, 0, 2.8, 2.3, and 1.9 respectively. The EXAFS model indicates that on the average each Pt atom in the cluster is bound to at least one oxygen atom of the support (NO =1.5). This is also consistent with a single layer of Pt atoms bound to the alumina surface.

In this paper we have describe the details of the EXAFS model used to accurately reproduce the measured Pt spectrum from reduced hydrogen saturated 0.4wt% Pt on γ-Al₂O₃. The small first shell coordination number of 4.4 ± 0.6 and the nearly zero 2nd shell CN are consistent with a 2-dimensional 13 atom cluster on the γ-Al₂O₃ support.
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Figure 2. Magnitude (A) and real part of Fourier transform of 300C-reduced (symbols) and model (solid). The inset shows a 13 atom Pt cluster that is consistent with the EXAFS data.