

Pt/ γ -Al₂O₃ Reduction and Cluster Evolution Characterized by Aberration-corrected STEM imaging and EXAFS

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Supported Pt clusters are important in a wide range of industrial catalytic applications, for example hydrogenation and dehydrogenation of hydrocarbons. Understanding the formation of Pt clusters during reduction, and the structure of the clusters, is thus of wide practical and fundamental interest. This paper uses recent improvements in instrumentation and modelling in STEM imaging and X-ray absorption spectroscopy (XAS) to investigate cluster formation and structural evolution of 0.35 wt% Pt from a chloride precursor on a γ -Al₂O₃ support, during treatment in H₂ for a range of reduction temperatures.

The initial phase, during which the Pt reduction is largely completed, extends from room temperature up to 350°C. In this low-temperature regime, XAS and STEM provide a consistent picture of direct reduction of the Pt precursor by reaction with hydrogen from the gas phase and initial cluster formation. XANES shows a decrease in intensity of the pre-peak on the Cl K-edge, which closely follows the Pt reduction observable via the decay of the Pt white line. These trends also closely track the H₂ uptake measured by temperature programmed reduction (TPR), which supports the direct reduction mechanism. Aberration-corrected STEM images of the Pt distribution in this temperature regime show a steady increase in the mean number of Pt atoms per particle, resulting in a mixture of 4-7 Å clusters and isolated atoms at 350°C, as shown in Fig. 1a. This is consistent with the XAS result of an average Pt 1st neighbor coordination number (Pt1 CN) of 4.3±0.5 at this temperature, with a bond length of 2.77 Å.

Trends in cluster evolution in the high temperature regime (>350°C) differ substantially from those in H₂ reduction at low temperature. The current XAS work, in agreement with others [1], shows a steady decrease in the Pt1 CN for treatments in H₂ above 350°C. After 700°C treatment, the average Pt1 CN has dropped to approximately 2.0. This appears to conflict with the expectation of particle sintering as temperature increases, and suggests that clusters may redisperse: a Pt1 CN of 2 would occur for a predominant 3-atom triangular Pt cluster morphology. The XAS also shows the appearance and steady increase in the CN of a long Pt-O bond of 2.5 Å, with CN increasing to ~2.0 at 700°C. While the XAS Pt1 CN suggests a decreasing cluster size, the aberration-corrected STEM image after 700°C treatment in Fig. 1b clearly shows that Pt clusters continue to evolve to larger sizes above 350°C, and reach an average particle size of 8.8 Å by 700°C. The large particle size determined by STEM and small Pt-Pt CN by XAS suggests that a central feature of the structure evolution in H₂ treatments above 350°C is the development of large internal strains which may reduce the CN measured by XAS [2].

Further insight into the Pt cluster morphology was obtained using an approach developed at UOP for determining cluster morphology using aberration corrected-STEM [3]. A cluster is first imaged at moderate magnification in order to measure its diameter. The cluster is then completely dispersed on the support using extended beam irradiation, which allows the number of atoms to be counted directly from a subsequent STEM image. Fig. 2 shows a plot of the number of atoms versus cluster diameter for a large number of clusters, on reduced and steamed samples. The solid lines in the plot correspond to various models, for which the particle diameter dependence on the number of atoms is different. The

experimental data for the individual clusters tend to indicate too few atoms for a hemispherical model, and are most consistent with a bilayer model.

The development of a more two-dimensional rather than hemispherical model in high temperature reduction of Pt/ γ -Al₂O₃ is consistent with the XAS result of an increasing Pt-O interaction after high temperature reduction, which suggests increased Pt interaction with the support. Details of the XAS data for higher coordination shells also support a planar structure. A flat morphology with strong support interaction also provides a plausible rationale for the development of strain leading to the anomalous decrease in the XAS Pt-Pt CN as the temperature is increased. This study provides an example of how use of complementary techniques can lead to a more complete understanding of structures of catalytic particles. Further progress in understanding the high-temperature structure evolution of Pt clusters on γ -Al₂O₃ would benefit from direct structural determination of individual clusters with aberration-corrected microscopy. Potential approaches to this, as well as associated challenges, will be discussed.

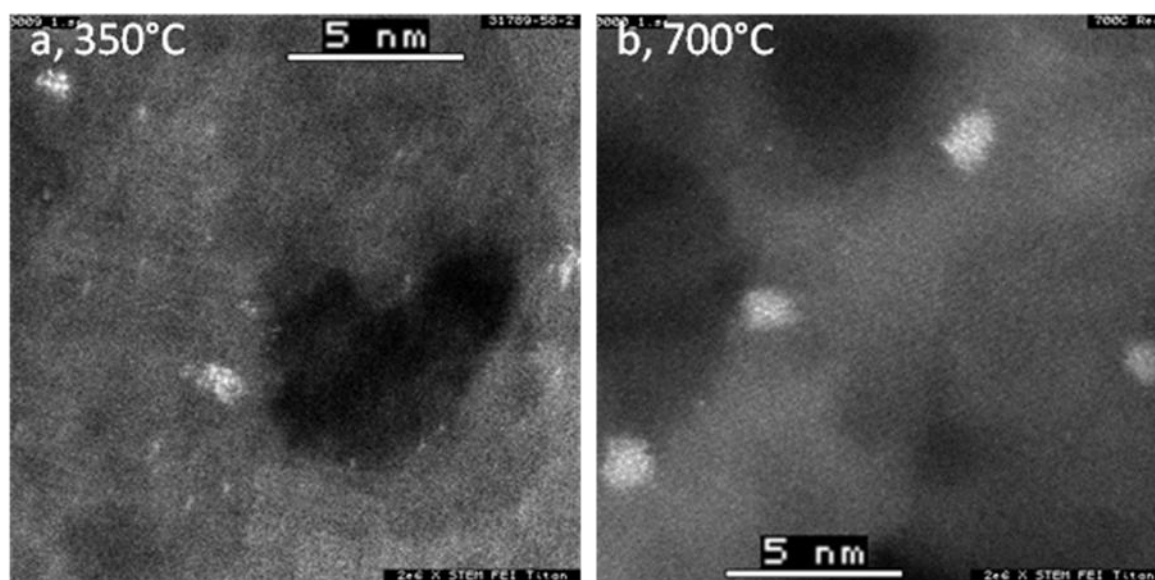


Fig. 1 Aberration corrected STEM images of 0.35 wt% Pt/ γ -Al₂O₃ at indicated temperatures

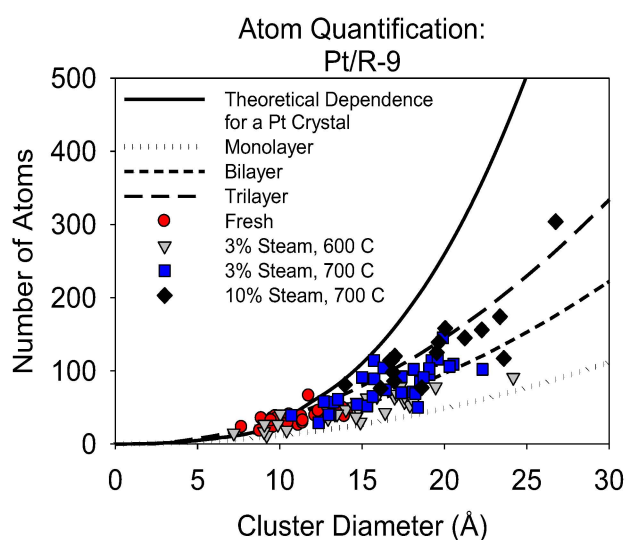


Fig. 2. Plot of number of atoms determined by STEM after particle dispersion, vs. initial cluster diameter.

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 [2] T. Shido and R. Prins, J. Phys. Chem B **102** (1998), p. 8426.
 [3] S. A. Bradley *et.al*, Catal. Lett. **142** (2012), p. 176.