

2007

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### Publication Info

*AIP Conference Proceedings*, 2007, pages 737-739.

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This article appeared in *AIP Conference Proceedings* and may be found at <http://link.aip.org/link/?APCPCS/882/737/1>.

DOI: 10.1063/1.2644648

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# EXAFS Characterization of Dendrimer-Derived Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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**Abstract.** The various steps involved in the preparation of a Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> material using hydroxyl-terminated generation four (G4OH) PAMAM dendrimers as templates were monitored by EXAFS. The results indicate that Cl ligands in the Pt precursors (H<sub>2</sub>PtCl<sub>6</sub> and K<sub>2</sub>PtCl<sub>4</sub>) were partially replaced by aquo ligands upon hydrolysis to form [PtCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> and [PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] species. After interaction of such species with G4OH, Cl ligands from the first coordination shell of Pt were further replaced by nitrogen atoms from the dendrimer interior, indicating the complexation of Pt with the dendrimer. This process was accompanied by a transfer of the electron density from the dendrimer to Pt, indicating that the former plays the role of a ligand. Following treatment of the H<sub>2</sub>PtCl<sub>6</sub>/G4OH and K<sub>2</sub>PtCl<sub>4</sub>/G4OH composites with NaBH<sub>4</sub>, no substantial changes were detected in the electronic or coordination environment of Pt, and no formation of metal nanoparticles was observed. However, when the reduction treatment was performed with H<sub>2</sub>, the formation of extremely small Pt clusters incorporating no more than 4 Pt atoms was observed. These Pt species remained strongly bonded to the dendrimer and their nuclearity depends on the length of the H<sub>2</sub> treatment. Formation of Pt nanoparticles with an average diameter of approximately 10 Å was finally observed after the deposition of H<sub>2</sub>PtCl<sub>6</sub>/G4OH on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and drying, suggesting that their formation may be related to the collapse of the dendrimer structure. The Pt nanoparticles formed appear to have high mobility, since subsequent thermal treatment in O<sub>2</sub>/H<sub>2</sub> led to further sintering.

**Keywords:** Dendrimers, Platinum, Nanoparticles, EXAFS.

**PACS:** 82.35.Np

## INTRODUCTION

The performance of supported metal catalysts depends on the structure and composition of the metal particles, and the nature of the support. Conventional preparation techniques provide limited control over the structure of the resulting materials. Alternative synthetic routes based on the use of templating agents, surfactants, and polymers have been proposed [1]. Among such templating materials, poly(amidoamine) dendrimers have attracted growing attention. The preparation of such metal-dendrimer nanocomposites carries similarities with the synthesis of colloids, and involves the complexation of metal cations with interior tertiary amine or amide groups, followed by the reduction of the metal cations and the formation of encapsulated nanoparticles [1-3]. Published UV-Vis [1], TEM [3], and SAXS [3] data indeed, appear to support the formation of metallic nanoparticles following the reduction step. Nevertheless, there is a lack of direct structural data in support of such a conclusion. Furthermore, little is known about the delivery of dendrimer-stabilized metal nanoparticles onto high surface area metal oxide supports, which is a necessary step during the synthesis of heterogeneous catalysts. Consequently, the goal of this work is to

develop a better molecular-level understanding of the preparation steps of Pt-dendrimer nanocomposites eventually used for the synthesis of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

## EXPERIMENTAL

Pt-dendrimer nanocomposites were prepared by complexation of Pt<sup>n+</sup> cations in aqueous solutions with interior functional groups of the G4OH dendrimer as described elsewhere [4]. The resulting complexes were purified by dialysis and treated with H<sub>2</sub> or NaBH<sub>4</sub> before impregnation on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Catalysts thus prepared were then treated in O<sub>2</sub>/He at 400°C for 1h followed by H<sub>2</sub> at 300°C for 2h to remove the dendrimer component.

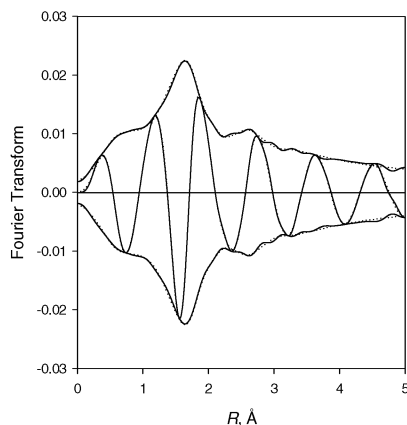
EXAFS spectra were collected at beamlines X-18B and 2-3 at NSLS and SSRL, respectively. The storage ring electron energies were 2.8 and 3 GeV, and the corresponding ring currents were 110-250 and 50-100 mA at NSLS and SSRL, respectively. The G4OH-Pt<sub>40</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples were loaded as wafers into an *in-situ* EXAFS cell and the data were recorded in the transmission mode at nearly liquid nitrogen temperature. The data for liquid samples were

collected at room temperature in the fluorescence mode with a 13<sup>th</sup> element Ge detector. In both cases, a Si(111) double-crystal monochromator was detuned by 40% to minimize the effects of higher harmonics in the X-ray beam. The Pt–Pt, Pt–N(O), Pt–Cl, and Pt–C interactions were analyzed with phase shifts and backscattering amplitudes obtained from EXAFS data of Pt foil, Na<sub>2</sub>Pt(OH)<sub>6</sub>, K<sub>2</sub>PtCl<sub>4</sub>, and Ir<sub>4</sub>(CO)<sub>12</sub>, respectively. The EXAFS parameters were extracted from the raw data with XDAP software [5]. A typical comparison of the data and fit in *r*-space is shown in Fig. 1.

## RESULTS AND DISCUSSION

### Characterization of H<sub>2</sub>PtCl<sub>6</sub> and K<sub>2</sub>PtCl<sub>4</sub> Before and After Complexation with G4OH

H<sub>2</sub>PtCl<sub>6</sub> is known to undergo a series of hydrolysis reactions in aqueous solutions, while the octahedral coordination of Pt (IV) remains intact [6]. Our EXAFS data for an aqueous solution containing 200 ppm of H<sub>2</sub>PtCl<sub>6</sub> at a pH of 2.7 indicate that the first coordination shell of Pt consists on average of 3±0.2 Cl atoms at a Pt–Cl distance of 2.31±0.02 Å and 3±0.3 oxygen atoms (representing aquo ligands) at a Pt–O distance of 2.01±0.02 Å. Hence, we can suggest that a [PtCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup>-type species dominates in this solution.



**Figure 1.** Results of EXAFS analysis of G4OH-(Pt<sup>2+</sup>)<sub>40</sub> treated with NaBH<sub>4</sub> in aqueous solutions: imaginary part and magnitude of uncorrected Fourier transform (*k*<sup>0</sup> weighted,  $\Delta k = 3.5\text{--}15.0 \text{ \AA}^{-1}$ ) of experimental EXAFS (solid line) and sum of the calculated contributions (dotted line).

Similar data collected for an aqueous solution containing 1500 ppm of K<sub>2</sub>PtCl<sub>4</sub> at a pH of 4.3 indicate that the first coordination shell of Pt consists on average of 2±0.1 Cl atoms at a Pt–Cl distance of 2.33±0.01 Å and 2±0.2 oxygen atoms at a Pt–O distance of 2.17±0.01 Å, suggesting that the planar

square PtCl<sub>4</sub><sup>2-</sup> complex also undergoes hydrolysis leading to the formation of [PtCl<sub>4-x</sub>(H<sub>2</sub>O)<sub>x</sub>]<sup>x-2</sup>-type species, consistent with previous literature reports [7].

When aqueous solutions containing Pt<sup>n+</sup> cations are brought in contact with G4OH, complexation of Pt<sup>n+</sup> with amide and/or amine groups from the dendrimer interior is expected to take place [2]. The EXAFS data obtained for G4OH-(Pt<sup>4+</sup>)<sub>40</sub> show that the first coordination shell of Pt consists of 2.2±0.1 Cl atoms at a Pt–Cl distance of 2.32±0.02 Å and 3.7±0.2 nitrogen (oxygen) atoms at a Pt–N(O) distance of 2.08±0.02 Å. A comparison of these data with those obtained for H<sub>2</sub>PtCl<sub>6</sub>/H<sub>2</sub>O allows us to conclude that at the completion of the complexation on the average one Cl ligand was replaced in the first coordination shell of Pt by nitrogen atoms of the amine or amide groups of the dendrimer. Moreover, the relatively high white line area observed for the H<sub>2</sub>PtCl<sub>6</sub>/H<sub>2</sub>O mixture decreased from 13.1 to 6.8 when G4OH was added to the solution, indicating that the dendrimer plays the role of a ligand, which is strongly bonded to Pt.

When K<sub>2</sub>PtCl<sub>4</sub> was used as the precursor, the complexation of Pt<sup>2+</sup> with G4OH appears to follow a mechanism similar to that observed for Pt<sup>4+</sup>. The EXAFS data collected for G4OH-(Pt<sup>2+</sup>)<sub>40</sub> indicate that on average only 0.3±0.1 Cl ligands at a *R*<sub>Pt–Cl</sub> distance of 2.32±0.02 Å remained in the first coordination shell of Pt after the completion of the complexation. At the same time, the total number of N(O) neighbors observed at a bond distance of 2.09±0.02 Å was increased on average to 3.7±0.2, indicating that the complexation with the dendrimer did not change the planar square geometry of Pt<sup>2+</sup>. In this case, no detectable changes were observed in the white line area, suggesting that the bonds between G4OH and Pt<sup>2+</sup> cations are weaker than those with Pt<sup>4+</sup>, or that the charge-transfer process is limited in this case.

### Treatment of G4OH-(Pt<sup>n+</sup>)<sub>40</sub> Complexes with Reducing Agents

When NaBH<sub>4</sub> was used to treat G4OH-(Pt<sup>4+</sup>)<sub>40</sub> or G4OH-(Pt<sup>2+</sup>)<sub>40</sub> solutions, the EXAFS and XANES results indicate the absence of any substantial changes in the coordination and electronic environment of Pt, suggesting that in both cases Pt remains strongly bonded to the dendrimer in cationic form and no nucleation of Pt takes place.

In contrast, the EXAFS analysis of the G4OH-(Pt<sup>4+</sup>)<sub>40</sub> aqueous solution treated with H<sub>2</sub> for 2 h indicates for the first time the presence of a relatively small Pt–Pt contribution with a coordination number of 1.3±0.1 at a bond distance of 2.76±0.01 Å. Furthermore, approximately 3.5±0.3 nitrogen/oxygen atoms were also present in the neighborhood of Pt at a

bonding distance of  $2.12 \pm 0.02$  Å, suggesting that Pt remained attached to the dendrimer following this treatment. When longer  $H_2$  treatment times were used, the value of  $N_{Pt-Pt}$  was further increased to  $2.6 \pm 0.2$  after 48 h and remained nearly unchanged thereafter, indicating the formation of small Pt clusters incorporating on average no more than 4 Pt atoms. The presence of  $3.4 \pm 0.2$  nitrogen/oxygen backscatters at a bonding distance of  $2.09 \pm 0.02$  Å indicates that these clusters remained in contact with the dendrimer. Since no substantial changes were observed in the white line area, we can suggest that these small Pt clusters remained strongly bonded to the dendrimer and did not undergo complete reduction under our experimental conditions.

### Deposition of $G4OH-(Pt^{4+})_{40}$ onto $\gamma-Al_2O_3$

When the  $H_2$ -treated  $G4OH-(Pt^{4+})_{40}$  aqueous solution was impregnated onto  $\gamma-Al_2O_3$  and the sample was dried by evacuation at  $25^\circ C$ , Pt–Pt contributions attributed to the first four coordination shells with respective  $N_{Pt-Pt}$  values of  $5.6 \pm 0.2$ ,  $3.4 \pm 0.3$ ,  $9.1 \pm 0.3$ , and  $6.3 \pm 0.3$  were detected, clearly demonstrating the formation of Pt nanoparticles under these conditions. These particles remain trapped by the dendrimer, as evidenced by the presence of Pt–N(O) and Pt–C contributions at  $2.03 \pm 0.02$  and  $2.14 \pm 0.03$  Å, respectively. The formation of Pt nanoparticles at this stage can be attributed to the removal of the solvent and the following configurational collapse of the dendrimer branches upon deposition on the support and drying. No Pt nanoparticles were formed following deposition on  $\gamma-Al_2O_3$  and drying of untreated  $G4OH-(Pt^{4+})_{40}$ , indicating that a previous treatment with  $H_2$  is necessary for Pt nanoparticle formation during impregnation.

### Removal of the Dendrimer Component

Following drying, the Pt nanoparticles trapped by the dendrimer are “shielded” from reactants and consequently are not catalytically active [4]. Therefore, dendrimer removal is an important step in the activation of the catalyst. Thus, the sample was treated at  $400^\circ C$  in a 10%  $O_2/He$  mixture for 2 h followed by reduction with  $H_2$  at  $300^\circ C$  to remove the dendrimer component. Such an oxidation-reduction treatment leads to an increase in the Pt–Pt first-shell coordination number from  $5.6 \pm 0.2$  to  $11.2 \pm 0.2$ . Calculated  $N_{Pt-Pt}$  values for the second, third, and fourth Pt–Pt shells were also increased to values of  $6.0 \pm 0.3$ ,  $15.4 \pm 0.3$ , and  $7.0 \pm 0.3$ , respectively, indicating substantial sintering of the Pt nanoparticles under these

conditions. Such sintering can be in part attributed to the high mobility of the dendrimer-covered Pt particles, implying that the efficient removal of the dendrimer without Pt sintering is a major challenge that remains to be solved.

## CONCLUSIONS

EXAFS was used to characterize and understand on a molecular level the preparation of supported Pt/ $\gamma-Al_2O_3$  catalysts via the use of  $G4OH$  dendrimer templates. The results indicate that the hydrolysis of  $H_2PtCl_6$  and  $K_2PtCl_4$  leads to the formation of  $[PtCl_3(H_2O)_3]^+$  and  $[PtCl_2(H_2O)_2]$  species, respectively. These species strongly interact with amine and/or amide groups in the interior of the dendrimer. Such interactions lead to transfer of electron density from the dendrimer to Pt and to the replacement of  $Cl^-$  ions by functional groups from the dendrimer, indicating that the dendrimer plays the role of a ligand. No substantial electronic or structural changes were observed when both  $G4OH-(Pt^{4+})_{40}$  and  $G4OH-(Pt^{2+})_{40}$  aqueous solutions were treated with  $NaBH_4$  at  $25^\circ C$ , indicating that complete reduction of the  $Pt^{n+}$  cations and the formation of Pt nanoparticles do not take place under these conditions. The formation of extremely small Pt clusters was observed when  $G4OH-(Pt^{4+})_{40}$  was treated with  $H_2$ . These clusters remained strongly bonded to the dendrimer and are most likely cationic in nature. The formation of Pt nanoparticles eventually took place following the impregnation of the  $H_2$ -treated  $G4OH-(Pt^{4+})_{40}$  on  $\gamma-Al_2O_3$  and subsequent drying, presumably because the removal of the solvent leads to the collapse of the dendrimer branches and clustering of the Pt cations. Subsequent thermal treatments in  $O_2/H_2$  leads to substantial sintering of the Pt particles, indicating that the Pt nanoparticles initially formed have high mobility on the dendrimer-support surface.

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