EXAFS Characterization of Dendrimer-Derived Pt/γ-Al₂O₃

A. Siani, O. S. Alexeev, C. T. Williams, H. J. Ploehn, and M. D. Amiridis

Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA

Abstract. The various steps involved in the preparation of a Pt/γ-Al₂O₃ 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 (H₂PtCl₆ and K₂PtCl₄) were partially replaced by aquo ligands upon hydrolysis to form [PtCl₂(H₂O)₃]⁺ and [PtCl₂(H₂O)₂]⁻ 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 H₂PtCl₆/G4OH and K₂PtCl₄/G4OH composites with NaBH₄, 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 H₂, 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 H₂ treatment. Formation of Pt nanoparticles with an average diameter of approximately 10 Å was finally observed after the deposition of H₂PtCl₆/G4OH on γ-Al₂O₃ 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 O₂/H₂ 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/γ-Al₂O₃ catalysts.

EXPERIMENTAL

Pt-dendrimer nanocomposites were prepared by complexation of Pt⁴⁺ 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 H₂ or NaBH₄ before impregnation on γ-Al₂O₃. Catalysts thus prepared were then treated in O₂/He at 400°C for 1h followed by H₂ 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-Pt⁴⁺/γ-Al₂O₃ 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 13th 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, Na₂Pt(OH)₆, K₂PtCl₄, and Ir₄(CO)₁₂, 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 H₂PtCl₆ and K₂PtCl₄ Before and After Complexation with G₄OH

H₂PtCl₆ 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 H₂PtCl₆ 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 [PtCl₃(H₂O)₃]⁺-type species dominates in this solution.

When aqueous solutions containing Ptⁿ⁺ cations are brought in contact with G₄OH, complexation of Ptⁿ⁺ with amide and/or amine groups from the dendrimer interior is expected to take place [2]. The EXAFS data obtained for G₄OH-(Pt⁴⁺)₄₀ 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 H₂PtCl₆/H₂O 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 H₂PtCl₆/H₂O 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 K₂PtCl₄ was used as the precursor, the complexation of Pt²⁺ with G₄OH appears to follow a mechanism similar to that observed for Pt⁴⁺. The EXAFS data collected for G₄OH-(Pt²⁺)₄₀ indicate that on average only 0.3±0.1 Cl ligands at a Rₚₐ-CI 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 Pt²⁺. In this case, no detectable changes were observed in the white line area, suggesting that the bonds between G₄OH and Ptⁿ⁺ cations are weaker than those with Pt⁴⁺, or that the charge-transfer process is limited in this case.

Treatment of G₄OH-(Ptⁿ⁺)₄₀ Complexes with Reducing Agents

When NaBH₄ was used to treat G₄OH-(Pt⁴⁺)₄₀ or G₄OH-(Pt²⁺)₄₀ 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-(Pt⁴⁺)₄₀ aqueous solution treated with H₂ for 2h 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±0.02 Å, suggesting that Pt remained attached to the dendrimer following this treatment. When longer H2 treatment times were used, the value of \(N_{\text{Pt-Pt}}\) was further increased to 2.6±0.2 after 48h and remained nearly unchanged thereafter, indicating the formation of small Pt clusters incorporated on average no more than 4 Pt atoms. The presence of 3.4±0.2 nitrogen/oxygen backscatterers at a bonding distance of 2.09±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-(Pt4+)40 onto γ-Al2O3**

When the H2-treated G4OH-(Pt4+)40 aqueous solution was impregnated onto γ-Al2O3 and the sample was dried by evacuation at 25°C, Pt–Pt contributions attributed to the first four coordination shells with respective \(N_{\text{Pt-Pt}}\) values of 5.6±0.2, 3.4±0.3, 9.1±0.3, and 6.3±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±0.02 and 2.14±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 γ-Al2O3 and drying of untreated G4OH-(Pt4+)40, indicating that a previous treatment with H2 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°C in a 10% O2/He mixture for 2h followed by reduction with H2 at 300°C to remove the dendrimer component. Such an oxidation-reduction treatment leads to an increase in the Pt–Pt coordination number from 5.6±0.2 to 11.2±0.2. Calculated \(N_{\text{Pt-Pt}}\) values for the second, third, and fourth Pt–Pt shells were also increased to values of 6.0±0.3, 15.4±0.3, and 7.0±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/γ-Al2O3 catalysts via the use of G4OH dendrimer templates. The results indicate that the hydrolysis of \(\text{H}_2\text{PtCl}_6\) and \(\text{K}_2\text{PtCl}_4\) leads to the formation of \(\left[\text{PtCl}_3\left(\text{H}_2\text{O}\right)_3\right]^+\) and \(\left[\text{PtCl}_2\left(\text{H}_2\text{O}\right)_2\right]\) 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-(Pt4+)40 and G4OH-(Pt2+)40 aqueous solutions were treated with NaBH4 at 25°C, indicating that complete reduction of the Ptn+ 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-(Pt4+)40 was treated with H2. 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 H2-treated G4OH-(Pt4+)40 on γ-Al2O3 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 \(\text{O}_2/\text{H}_2\) leads to substantial sintering of the Pt particles, indicating that the Pt nanoparticles initially formed have high mobility on the dendrimer-support surface.

**REFERENCES**