

PAMAM Dendrimers as Templates for the Preparation of Supported Pt and Rh Catalysts

Attilio Siani,¹ D. Samuel Deutsch¹, Oleg S. Alexeev,¹ Gwendoline Lafaye², Paul T. Fanson,³ Hirohito Hirata⁴, Shinichi Matsumoto⁴, Harry J. Ploehn¹, Christopher T. Williams, and Michael D. Amiridis*¹

¹Department of Chemical Engineering
University of South Carolina, Columbia, SC 29208 (USA)

²Laboratoire de Catalyse en Chimie Organique,
UMR CNRS 6503 Université de Poitiers, Poitiers Cedex, F-86022 (France)

³Toyota Motor Engineering and Manufacturing, Inc., Ann Arbor, MI 48105 (USA)

⁴Toyota Motor Corporation, Higashi-Fuji Technical Center, Shizuoka, 410-1193 (Japan)

*amiridis@enr.sc.edu

Introduction

Conventional methods used for the preparation of supported catalysts often provide limited control over the structure and composition of the resulting materials. In recent years, alternative synthetic routes based on the use of templating materials capable of stabilizing nanoparticles of various metals in solutions have been proposed [1]. Among such templating materials, poly (amidoamine) (PAMAM) dendrimers have attracted growing interest due to the potential for a tight control of the average metal particle size and distribution in the resulting catalysts. The preparation of metal-dendrimer nanocomposites bears similarities to the synthesis of colloids and involves the complexation of metal cations with interior tertiary amine or amide groups of the dendrimers, followed by a reduction step during which the formation of metal nanoparticles, encapsulated within the dendrimer structure, is anticipated [2]. However, a lack of direct structural data showing the formation of the dendrimer-encapsulated nanoparticles raises questions about the proposed templating mechanism. Furthermore, little is known about the delivery of dendrimer-stabilized metal nanoparticles onto metal oxide surfaces, a necessary step during the synthesis of heterogeneous catalysts. Our goal is to develop a better molecular-level understanding of the processes taking place during the synthesis of (Pt, Rh)-PAMAM nanocomposites used as precursors for the preparation of supported catalysts. HRTEM and EXAFS were used for the characterization of such materials during the various preparation steps and the data indicate that highly dispersed Rh/ZrO₂ catalysts with narrow distribution of Rh particles and improved catalytic properties can be successfully prepared via the dendrimer synthetic route.

Materials and Methods

Pt- and Rh-dendrimer nanocomposites were prepared by complexation of Pt⁴⁺ and Rh³⁺ cations with the interior functional groups of G4OH dendrimers. Following the complexation, the solutions were dialyzed and subsequently treated either with H₂ or NaBH₄ at 25 °C. Supported samples were prepared by slurring of the reduced Pt-DMNs and Rh-DMNs solutions with γ -Al₂O₃ and ZrO₂, respectively, in amounts chosen to yield samples containing 1 wt % of each metal. The solid samples were subjected to oxidation and reduction treatments to remove the dendrimer shell and activate the metal components. EXAFS spectra were collected at beamline 2-3 at SSRL. TEM imaging was performed with a high-resolution Hitachi HF-2000 instrument at ORNL.

Results and Discussion

The EXAFS results indicate that the hydrolysis of H₂PtCl₆ and RhCl₃ leads to the formation of [PtCl₃(H₂O)₃]⁺ and [RhCl₃(H₂O)₃] species, respectively. These species can strongly interact with amine/amide groups of the dendrimer as evidenced by the replacement of chlorine ligands from the first coordination shell of each metal by nitrogen atoms from the dendrimer interior. In the case of Pt, this process was also accompanied by a substantial transfer of the electron density from the dendrimer to the metal, indicating that the dendrimer plays the role of a ligand. Following treatment of the Pt⁴⁺-G4OH complexes with NaBH₄, no substantial changes were observed in the electronic and coordination environment of Pt, indicating that metal nanoparticles were not formed during this step under our experimental conditions. The formation of small Pt clusters incorporating on average no more than 4 atoms was observed when Pt⁴⁺-G4OH was treated with H₂ for several hours. The nuclearity of these small Pt clusters – which remained strongly bonded to the dendrimer – depends on the length of the hydrogen treatment. The formation of larger Pt nanoparticles, with an average diameter of approximately 1 nm, was finally observed after the deposition and drying of the H₂-treated Pt⁴⁺-G4OH nanocomposites on a γ -Al₂O₃ surface, suggesting that the formation of such nanoparticles may be related to the collapse of the dendrimer structure.

A different pattern was observed with the Rh samples. In this case, the formation of small Rh clusters with a nuclearity of 3 was observed after the treatment of Rh³⁺-G4OH with NaBH₄ at 25°C. Subsequent deposition of the NaBH₄-treated Rh³⁺-G4OH on the ZrO₂ surface does not lead to any substantial modifications of the Rh coordination environment. Sintering of the metal particles was observed with both metals following thermal treatments in O₂/H₂, indicating that the metal nanoparticles have relatively high mobility on the dendrimer surface. However, the degree of such sintering in the case of Rh was minimal, leading to highly dispersed Rh/ZrO₂ catalysts with extremely narrow particle size distributions. The kinetic behavior of such catalysts in the structure sensitive reaction of ethane hydrogenolysis is consistent with the presence of rhodium particles with an average diameter below 1 nm. Such highly dispersed Rh showed improved catalytic performance for the oxidation of CO and the reduction of NO by CO, as compared to samples prepared by conventional techniques and showing broader distribution of metal particle sizes.

Significance

This work represents a first attempt to monitor changes in the coordination environment of Pt and Rh atoms during the different preparation steps of dendrimer-derived supported catalysts. The results challenge existing notions in the field and suggest that contrary to what was believed so far, metal nanoparticles are not formed in the liquid phase. However, depending on the nature of the metal and the support used, highly dispersed supported catalysts with narrow particle size distributions can be prepared via the dendrimer synthetic route. The catalytic properties of such materials are different from those of conventionally prepared catalysts for certain reactions including the oxidation of CO and the reduction of NO by CO.

References

1. Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* 120, 4877 (1998).
2. Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. *J. Phys. Chem. B* 109, 692 (2005).