

Synthesis and Characterization of PAMAM-OH Dendrimer-Derived Iridium Supported Catalysts

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Introduction

Conventional synthetic approaches for supported metal catalysts often result in wide particle size distributions, and such non-uniform materials can be difficult to characterize on a fundamental level. Dendrimer-metal nanocomposites (DMNs) provide a novel synthetic route that has been used to produce heterogeneous catalysts [1]. These and other findings have demonstrated that control of metal nanoparticle size and distribution can be obtained even after thermal removal of the dendrimer “shell” [1]. Supported iridium catalysts possess unique properties that can enhance activity and selectivity for a variety of reactions, including hydrogenation [2]. Here we report for the first time the synthesis of supported monometallic and bimetallic iridium catalysts using DMN precursors. The catalysts have been characterized using several different techniques, including HRTEM, FTIR, and EXAFS, and evaluated kinetically for liquid-phase benzonitrile hydrogenation.

Materials and Methods

Fourth generation hydroxyl-terminated (G4OH) polyamidoamine (PAMAM-OH) dendrimer was combined with $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ at various metal-dendrimer molar ratios in aqueous solution under N_2 atmosphere at room temperature. The Ir-dendrimer complexation process was monitored via ultraviolet-visible (UV-Vis) spectroscopy. Ir-DMNs complexes were further treated in solution either with H_2 or NaBH_4 at room temperature and examined using X-ray absorption near edge spectroscopy (XANES) and UV-Vis. The Ir-DMNs precursor was wet impregnated onto a calcined $\gamma\text{-Al}_2\text{O}_3$ ($45 \text{ m}^2/\text{g}$) up to 1 wt% Ir. Dendrimer thermal decomposition was performed under He , O_2 and H_2 flows and monitored by Fourier transform infrared (FTIR) spectroscopy. High resolution transmission electron microscopy (HRTEM) was used to measure particle size distributions, while extended X-ray absorption fine structure (EXAFS) spectroscopy was used to determine the local environment of Ir. Various dendrimer-derived Ir-Pd bimetallic catalysts were synthesized from PdCl_2 and IrCl_3 precursors using either co-complexation or sequential complexation methods. All catalysts were tested for liquid-phase benzonitrile hydrogenation in ethanol at 300psi and 100°C using an autoclave reactor.

Results and Discussion

UV-Vis time-dependent spectra for dendrimer-Ir mixtures show gradual changes occurring over several days, with a complete complexation achieved after 7 days. The reduction of iridium was not accomplished using either H_2 or NaBH_4 . Therefore, no formation of iridium nanoparticles in solutions, as suggested previously, was observed [3]. The dendrimer decomposition experiments performed with the 1 wt% $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$ sample suggested

that the dendrimer shell can be removed efficiently under oxidative or reductive environments at elevated temperatures. *In-situ* FTIR monitoring of the CO adsorption was used to determine optimal activation protocols. When the treatment of this sample with O_2 at 350°C for 30 min was followed by H_2 at 400°C for 1 h, an average Ir particle size was found to be 1.2 nm, which corresponds to approximately 97% of the metal dispersion (Fig. 1). In contrast, when the same sample was treated directly in H_2 at 400°C for 2 h, an average size of Ir particles was found to be 1.5 nm and the metal dispersion was 78%. For comparison, similar catalysts prepared by wet impregnation (i.e. without the dendrimer) yielded an average Ir particle size of approximately 1.2 nm regardless of the activation treatment used. These results combined with the EXAFS data obtained for all mentioned samples suggest that the DMNs can serve as templates to control particle sizes of supported metals by varying treatment protocols.

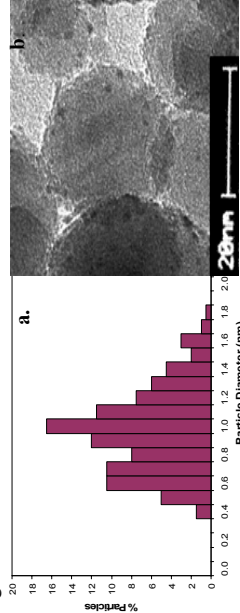


Figure 1. a) Particle size distribution and b) representative HRTEM image of DMN-derived 1 wt% $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$ after the O_2/H_2 treatment.

Benzonitrile hydrogenation was used as a test reaction to examine the catalytic activity and selectivity of monometallic and bimetallic DMNs-derived catalysts. Dibenzylamine was a favored product for $\text{Ir}/\text{Al}_2\text{O}_3$, whereas $\text{Pd}/\text{Al}_2\text{O}_3$ selectively produced benzylamine. The activity of Pd catalysts was 3–4 times higher than that of Ir, and this trend was observed for both conventional and DMN-derived catalysts. However, the conventional and DMN-derived catalysts show different product selectivities, with the former selectively producing the primary amine and the latter forming the secondary amine. The results suggest that the DMN-derived bimetallic precursors either form different bimetallic structures or distributions of metallic particles relative to those formed by conventional methods of preparation.

Significance

These results expand further the range of metals for which the DMN preparation approach appears to be feasible. The results obtained for DMN-derived bimetallic Ir-Pd catalysts suggest that this preparation approach can be used to alter properties of bimetallic catalytic to a significant extent.

References

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