

## Dendrimer-Derived Ir-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts

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### Introduction

Supported bimetallic catalysts prepared by conventional methods often result in wide particle size distributions and non-uniform materials which can be difficult to characterize on a fundamental level. Dendrimer-metal nanocomposites (DMN) provide a novel synthetic route that has been used to produce heterogeneous catalysts [1]. These and other findings have demonstrated that control of bimetallic particle composition and particle size distribution can be obtained even after thermal removal of the dendrimer “shell” [1]. Supported Ir and Pd catalysts possess unique properties that can enhance activity and selectivity for a variety of reactions, including hydrogenation. We report for the first time the synthesis of supported bimetallic Ir-Pd catalysts using DMN precursors. These catalysts have been characterized using several different techniques, including STEM, FTIR, EXAFS, H<sub>2</sub> chemisorption, temperature programmed methods and evaluated kinetically for liquid-phase benzonitrile hydrogenation.

### Materials and Methods

Fourth generation hydroxyl-terminated polyamidoamine dendrimer was combined with IrCl<sub>3</sub>•H<sub>2</sub>O and PdCl<sub>2</sub> in aqueous solution under N<sub>2</sub> atmosphere at room temperature. Three different bimetallic compositions were examined while a total of 40:1 metal-to-dendrimer molar ratio was kept constant. DMN precursors were prepared by two different methods. First, by sequential complexation, where Ir was introduced first since its complexation takes 7 days while for Pd takes 1 day and afterwards Pd become unstable. The second method consists of complexing each metal with dendrimer in separate solutions and mixing them together. These DMN solutions were deposited onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Alfaesar) via a standard wet impregnation at room temperature. The catalysts were then treated using the optimum O<sub>2</sub>/H<sub>2</sub> activation treatment reported elsewhere [2].

CO adsorption onto the bimetallic catalysts was monitored using in-situ FTIR spectroscopy to characterize active metallic surface species. STEM and EDX spectroscopy were used to measure particle size distributions and bimetallic particle compositions, respectively. In addition, EXAFS spectroscopy was used to determine the local environment of Ir and Pd. Furthermore, these catalysts were evaluated for liquid-phase benzonitrile hydrogenation in ethanol at 300 psi and 100 °C using an autoclave reactor along with conventionally prepared catalysts.

### Results and Discussion

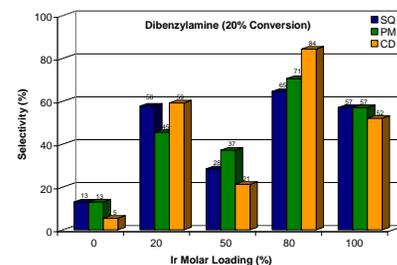
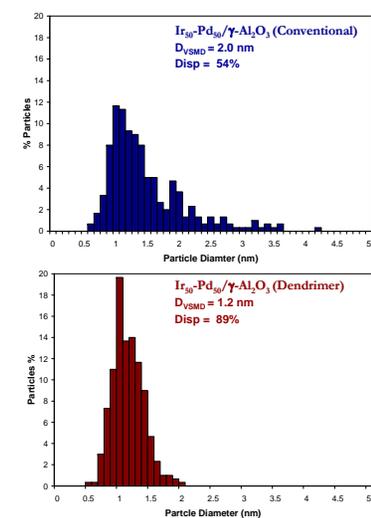
FTIR results show that the supported catalysts prepared using DMN precursors have active metallic surface sites capable of bonding CO molecules, just as their conventional

counterparts. However, different types of CO are adsorbed depending on the preparation method such as linear CO, gem dicarbonyl, and bridge CO on different metallic faces.

The average particle diameter increases as the Pd content increases for conventional bimetallic catalysts. However, the particle size is less variable with Pd content when DMN precursors are used. Furthermore, dendrimer-derived (DD) catalysts prepared by co-impregnation of monometallic Ir-DMN and Pd-DMN precursors have smaller particle size the narrowest particle size distribution. Therefore, DMN precursors can be used to avoid sintering of the bimetallic nanoparticles (right).

Benzonitrile hydrogenation was used as a probe reaction to examine the catalytic activity and selectivity of monometallic and bimetallic DMN-derived catalysts. DD Ir and Pd catalysts have an initial TOF 2 times higher than the conventional monometallic catalysts. Monometallic Ir selectively produces

dibenzylamine whereas Pd favored the production of benzylamine. The bimetallic catalysts have different TOF magnitudes and selectivity (below left) depending on the bimetallic



composition. The results suggest that the DMN-derived precursors form different bimetallic structures. These results combined with the EXAFS data obtained suggest that the DMN can serve as templates to control both particle size and the catalytic properties of supported bimetallic nanoparticles.

### 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 bimetallic catalytic properties to a significant extent.

### References

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