Characterization and kinetic evaluation of dendrimer-derived Pt-Ru/SiO\textsubscript{2} catalysts for selective hydrogenation of 3,4-epoxy-1-butene

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Introduction  
Dendrimers are mono-disperse hyper-branched polymers that emanate from a central core with repetitive branching units. The use of dendrimers as templates/stabilizers for synthesis of encapsulated nanoparticles is a relatively new but active field. One of the more successful applications along these lines has been the synthesis of metal nanoparticles using poly-(amidoamine) (PAMAM) dendrimers. The approach takes advantage of the fact that transition metal ions (e.g., Pt\textsuperscript{2+}, Cu\textsuperscript{2+}, and Pd\textsuperscript{2+}) can coordinate with the interior amine groups of the dendrimer [1]. Such ions may then be reduced to form encapsulated metal nanoclusters or particles. Metal nanoparticles synthesized in this fashion have been demonstrated to exhibit interesting catalytic properties [2, 3]. The dendrimer can exert control over size and (in the case of multiple metal ions) composition of nanoparticles, which can allow for tuning of catalytic properties. In this presentation, we will address the characterization and kinetic evaluation of a series of PAMAM G4OH dendrimer derived PtRu catalysts supported on silica for selective hydrogenation of 3,4-epoxy-1-butene (EpB).

Materials and Methods  
Generation 4 PAMAM-OH dendrimer is allowed to complex with metal precursors (e.g., H\textsubscript{2}PtCl\textsubscript{6}, RuCl\textsubscript{3}) in aqueous solution having dendrimer/metal atom ratio = 1/40. This is followed by reduction using NaBH\textsubscript{4} to produce nanoparticles and/or clusters with controlled size, shape and composition. The co-complexation method involved adding the two metal precursor solutions simultaneously to the dendrimer solution, followed by reduction with NaBH\textsubscript{4} upon completion of the complexation. The sequential method involved complexing of one metal precursor solution with dendrimer after the other, with a reduction step in between. Dendrimer-metal nanocomposites were deposited onto silica support, and activated in flowing H\textsubscript{2} at 300 °C for 2 hours. The structure and electronic properties of the nanoparticles are examined with HRTEM, EDS, and XRD. Metal surface compositions were measured by temperature programmed H\textsubscript{2} titration of precovered oxygen. Selective hydrogenation of 3,4-epoxy-1-butene (EpB) was performed in a semi-batch autoclave reactor at 80 °C and 300 psig. The liquid reaction mixture was sampled at different times and analyzed by gas chromatography.

Results and Discussion  
The dendrimer-derived bimetallic catalyst by co-complexation method has significantly higher EpB initial conversion rate than others, as shown in Figure 1. In addition, higher instantaneous selectivity to crotonaldehyde, an intermediate product, were observed (Figure 2). This indicates that the reaction pathway is changed toward crotonaldehyde, as opposed to the 3-buten-1-ol route on other catalysts. Comparison of the experimental results to that expected with a simple mixture of monometallic sites, indicates a synergic effect on activity. This effect is attributed to PtRu dual sites that provide a more intimate and even distribution of Pt and Ru sites on the bimetallic surfaces. Existence of such a bimetallic alloy has been demonstrated by a significant shift to higher Bragg angles and an apparent broadening of the Pt peak widths in its XRD diffraction pattern. On the contrary, either slight or no shift was noticed in the other two bimetallic PtRu catalysts. TPD of crotonaldehyde shows that the largest amount was also desorbed from co-complexation PtRu catalysts. This confirms the enhanced strength and amount of crotonaldehyde adsorption on these PtRu sites that facilitated the EpB conversion via that intermediate. However, while the catalytic effects are substantial, based on the current findings we are not able to distinguish whether the key bimetallic interactions involve ensemble, electronic or bifunctional effects.

Significance  
These findings show conclusively that PAMAM dendrimers provide a promising route for synthesis of true bimetallic Pt-Ru catalysts that may provide enhanced control over traditional incipient wetness methodology.

References  