

#### **4cs Effect of Site-Isolation on the Preparation and Performance of Silica-Immobilized Cgc-Inspired Olefin Polymerization Catalysts**

*Michael W. McKittrick*

The major goals of this work were to: develop a new methodology for the preparation of site-isolated catalytic sites on a silica surface, prepare the first truly single-site supported metallocene/CGC polymerization catalyst, and develop structure-reactivity relationships for these new systems.

To synthesize these novel catalysts, the approach taken was to develop a protocol which allows for the synthesis of an aminosilica material with isolated, uniform amine sites. This patterned aminosilica was then used as a scaffold to support a constrained geometry catalyst. These functionalizations occurred at essentially a quantitative level, in stark contrast to previous literature reports. The patterned catalysts were evaluated in the polymerization of ethylene and compared to densely loaded literature materials. Overall, it was found the patterned materials were 5-10 times more active than traditional immobilized CGC catalysts.

The patterned catalysts were also found to be effective catalysts for the copolymerization of norbornenes (including functionalized norbornenes) and ethylene, the first reported use of a tethered CGC for the production of ethylene-norbornene copolymers. The control materials were inactive in these polymerizations, providing further evidence that the patterning protocol allows for the synthesis of unique highly active, isolated catalytic sites.

Various structural components of the immobilized CGC developed in this work were tested for their impact on catalyst synthesis and reactivity in ethylene polymerizations. The results showed the patterned materials in general behaved according to the trends seen in homogeneous CGC polymerizations. These results, while congruent with similar homogeneous CGC studies, are in direct conflict with previous work on supported CGCs reported in the literature. This discrepancy is likely the result of the difference between the isolated, possibly single-site patterned catalysts developed in the course of this work and the multi-sited catalysts prepared by traditional supporting protocols. This also further illustrates the difficulty in developing structure-reactivity relationships when ill-defined solid catalysts are used.