CHARACTERIZATION OF THE ACTIVE SITE IN THE PHILLIPS ETHYLENE POLYMERIZATION CATALYST

C.H. Brown (FSU, Chemistry); J. Krzystek (NHMFL); A. E. Stiegman (FSU, Chemistry)

Introduction
The Phillips ethylene polymerization catalyst is of industrial importance because it is used for the production of high density polyethylene. It is scientifically interesting because despite its industrial importance and nearly fifty years of research, the formation of the active site and the mechanism of polymerization is still not well understood. The precursor of the active catalyst is a chromium (VI) dioxo species, \((\text{SiO})_2\text{CrO}_2\) dispersed on silica. The active catalyst is formed from the reduction of this site either by ethylene itself (in the industrial process) or in the laboratory by gaseous reductants such as CO. The nature of the species that form as a result of the reduction processes are of interest in characterizing the active sites in polymerization reactions. It has long been thought that the reduction takes place in two stages, the first going from \(\text{Cr(VI)}\) to \(\text{Cr(IV)}\) and the second going from \(\text{Cr(IV)}\) to \(\text{Cr(II)}\) with the \(\text{Cr(II)}\) site being the active polymerization catalyst.

Experimental
Our experimental methodology was to utilize optical quality monolithic Cr(VI)/silica xerogel materials. For the reduction of chromium (VI) to lower oxidation states the monoliths were loaded into a closed spectroscopy cell where they can be heated under a flow of CO. The spectral changes were monitored in situ by UV-visible spectroscopy. Monitoring the reaction in situ allows for very consistent and reproducible results with a well-defined endpoint for reduction. After reduction the samples were removed from the cell under anhydrous and anaerobic conditions and prepared for other characterization. In particular, the samples were ground up and placed in an EPR cell for high-field EPR measurements.

Results and Discussion
It has long been thought that chromium (II) is the lowest oxidation state reached before formation of the catalytic active site. The evidence to support it rests largely on magnetic susceptibility measurements, which can be ambiguous if multiple oxidation states are present and electronic spectroscopy which, likewise, is a poor characterization method in the absence of appropriate model structures for comparison. EPR has also been a challenge since under normal X & Q band frequencies Cr(II) is silent due to the large zero-field splitting, which exceeds the microwave quantum of energy. Fortunately High-Frequency and -Field EPR (HFEPR) spectroscopy does not have the same limitations and allows the chromium (II) site to be observed. Using a 3 mol\% chromium sample that had been reduced at 350 °C, the HFEPR experiments were performed at 105.6, 212, and 317GHz and 10K and 20K to find the conditions that gave the best signal to noise. With the optimal setting obtained, the HFEPR spectrum (Fig. 1) was collected at 105.6GHz and at 10K. The simulation is a powder-pattern simulation that uses the following spin Hamiltonian parameters: \(S=2\), \(D=-2.06\ \text{cm}^{-1}\), \(E=0\), and \(g=1.99\). It should be noted that the simulation has ignored the peaks in the center of the graph, near approximately \(g=2\) because the program is designed to simulate only \(S=2\) non-Kramers atoms. The rest of the spectrum consists of several species that are positioned far enough away from the \(g=2\) to suggest that these belong to a non-Kramers species and a large zero-field splitting. The experimental spectrum compares very well with the simulation and published data for chromium (II) peaks.

Conclusions
This study represents this first unambiguous assignment of Cr(II) as the oxidation state attained before formation of the active site of the Phillips ethylene polymerization catalyst.