

The Active Site of the Phillip's Ethylene Polymerization Catalyst

Carole Brown¹, Melissa Mileham¹, Jerzy Krzystek², Randall Achey¹, Riqiang Fu², Robert W. Meulenberg³, A. E. Stiegman^{1*}

¹Dept. Of Chemistry and Biochemistry Florida State University, Tallahassee, Florida 32306 (USA)

²National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306(USA)

³Materials Science & Technology Division, Lawrence Livermore National Laboratory, Livermore, CA 94550 (USA)
*stiegman@chem.fsu.edu

Introduction

The Phillips ethylene polymerization catalyst has been a primary route to the commercial production of high-density polyethylene since Hogan and Banks patented it in 1958. Even today, it still accounts for approximately 30% of world production.¹ The Phillips catalyst is a single-site supported catalyst, initially made by the dispersion of Cr(VI) ions on silica. The active catalyst itself is formed by the reduction of the Cr(VI) at elevated temperatures. Industrially this is carried out using ethylene itself as the reductant, which gives rise to an induction period before polymerization begins. It can also be independently reduced using CO, which is more often done in laboratory studies. Due to its industrial importance, the Phillips catalyst has been studied extensively over the years and many of the parameters that effect the production of ethylene are understood. What has never been elucidated, however, is the actual active site of the catalyst and, hence, the mechanism by which ethylene is polymerized. We report the elucidation of the active site of the catalyst and key steps in its formation.

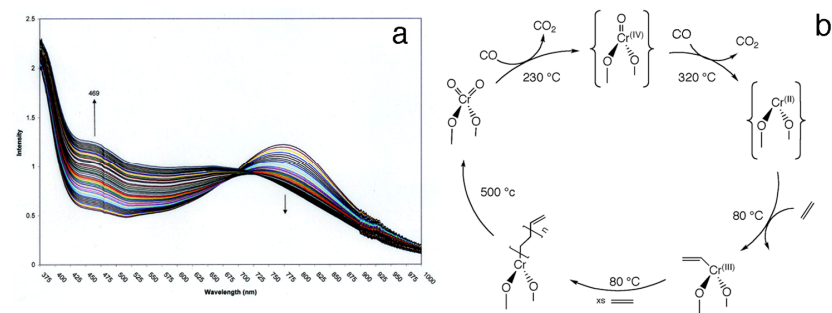
Materials and Methods

By utilizing sol-gel chemistry we formed the Philip's catalyst as a microporous optically transparent monolith. As initially established by us, these transparent monoliths provide a unique matrix with which to study heterogeneous reactions.² The optical transparency allows the reaction to be monitored using UV-vis spectroscopy in transmission mode. The microporous nature of the matrix allows only very slow diffusion of reaction, which slows down the process and allows intermediates to be formed stoichiometrically, isolated and studied. This approach for monitoring the reaction, coupled with the use of high-field/high-frequency electron paramagnetic resonance (HF-EPR) and solid-state nuclear magnetic resonance (NMR) spectroscopy ultimately facilitated the characterization of key intermediates in the process.

Results and Discussion

With this matrix we were able to monitor, in-situ, the sequential reduction of the Cr(VI) to Cr(IV) and ultimately to Cr(II). The Cr(II) site, which has long been postulated as the endpoint of the reduction, was directly observed and characterized by HF-EPR spectroscopy. Under

conditions of ethylene polymerization, the so-generated Cr(II) was titrated with stoichiometric amounts of ethylene (Figure 2a). The titration is nearly isobestic and at the endpoint, the C:Cr ratio was 1.75:1, consistent with approximately one ethylene per Cr ion. The oxidation state of the resulting complex is Cr(III) as determined by x-ray absorption near edge spectroscopy (XANES) and by HF-EPR which verified the disappearance of Cr(II) and the appearance of Cr(III). Characterization of the organometallic Cr(III) species was carried out by solid state



NMR which showed two distinct resonances of approximately equal intensity at ~75 and 146 ppm (relative to TMS) consistent with an intact ethylene group. Further verification of this structural assignment was carried out by a dephasing study, which eliminated the possibility of methylene groups being present (i.e. an aliphatic Cr(III)-CH₂CH₃). As such, the active site is assigned to Cr(III) with a sigma-bound vinyl group: Cr(III)-CH=CH₂. To establish that bulk polymerization can occur through this group, it was generated cleanly through titration. After it was generated, ethylene gas was introduced under condition used in ethylene polymerization. The subsequent formation of polyethylene in the matrix was characterized by vibrational spectroscopy. The overall mechanism deduced from the studies is shown shown figure 5b. The result explains the origin of the terminal vinyl group found in polyethylene produced from the Phillips catalyst, which has typically been attributed to β -hydrogen elimination during chain termination. A question that remain is the mechanism by which the Cr(II) species is oxidized to the observed Cr(III)-vinyl site. Current work indicates that it goes through a transitory Cr(IV) species that reductively eliminates hydrogen to go to Cr(III).

Significance

This study provides a comprehensive mechanism for the polymerization of ethylene through the Phillips catalyst. It represents a solution to a long-standing problem in heterogeneous catalysis.

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References

1. Groppo, E., Lamberti, C., Bordiga, S., Spoto, G., Zecchina, A., *Chem. Rev.* 105, 115 (2005).
2. Brown, C., Achey, R., Fu, R.Q., Gedris, T., and Stiegman, A.E., *J. Am. Chem. Soc.* 127, 11590 (2205).

