

The mechanism of self-initiation in the Phillips ethylene polymerization catalyst

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Abstract:

The mechanism of spontaneous activation of the Phillips (Cr/SiO_2) ethylene polymerization catalyst in the absence of an alkylating co-catalyst is one of the longest-standing problems in heterogeneous catalysis. While well-defined organochromium complexes have shed much light on their potential as homogeneous, single-site catalysts, no molecular complex reproduces the polymerization behavior and generates polyethylene that truly resembles that of the industrial heterogeneous Phillips catalyst (Cr/SiO_2). This implies that the silica support must be part of any active site model. Experimental and computational evidence has long pointed to organochromium(III) active sites. Grafting $\text{Cr}[(\text{CH}(\text{SiMe}_3)_2)_3]$ onto silica generates an ethylene polymerization catalyst with high activity, producing polymer that closely resembles Phillips polyethylene, and thus has active sites that closely resemble those of the Phillips catalyst. To investigate the nature of these sites, $[(\equiv\text{SiO})_2\text{Cr}(\text{CH}(\text{SiMe}_3)_2)]$ was prepared via reaction of the organochromium complex with silica. Elemental analysis shows that just one R ligand is retained per grafted Cr(III) site. The X-ray absorption spectra and DFT modeling are consistent with four-coordinate Cr(III), suggesting coordination of an additional O-donor ligand derived from the silica surface. The supported organochromium catalysts spontaneously initiate polymerization of gas phase ethylene at low pressure (ca. 130 Torr), in reactions that are first-order in both $P(\text{C}_2\text{H}_4)$ and moles of Cr.

However, a plausible mechanism for the formation of such sites solely from the interaction of chromate and ethylene alone remains to be found. A key issue is the incommensurate nature of the required redox reactions, since Cr(VI) must be reduced by an odd number of electrons (three), while only closed-shell organic oxidation products are detected. For the CO-reduced catalyst, Cr K-edge XANES, EPR and UV-vis spectroscopies are consistent with initial step-wise reduction of Cr(VI) in two-electron steps, first to Cr(IV), and ultimately to Cr(II). According to Cr K-edge EXAFS and UV-vis spectroscopy, the Cr(II) sites have a coordination number higher than two, most likely through interaction with neighboring siloxane oxygens. After removal of adsorbed CO, the Cr(II) sites react with ethylene via a two-step mechanism. Computational analysis suggests that the most likely path is initial reaction with two equiv. ethylene to produce (ethenyl)(ethyl)chromium(IV) sites via concerted hydride transfer, followed by silica-assisted Cr-C bond homolysis to generate organochromium(III) sites and ethyl radicals which dimerize to give n-butane.