

50 Years of Mechanistic Insight Into Phillips Catalyst

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Plastic is ubiquitous in our society, providing the cheap physical structure for many small objects. One of these commercially available polymers is polyethylene. While polyethylene can be made without a catalyst, it is very flimsy and stretchy, known as Low Density Polyethylene (LDPE). It wasn't until 1951 that a chromium based heterogeneous catalyst was discovered by Robert Banks and Paul Hogan at Phillips Petroleum, thus named the Phillips catalyst, that could make the stronger version called High Density Polyethylene (HDPE).¹ Currently this catalyst produces over half of the 57 million² tons of HDPE plastic made every year for our industrialized society. Synthesis of the Phillips catalyst is made by incorporating $\text{Cr}(\text{OAc})_3$ on a silica support and subsequently calcining it. Upon exposure to ethylene there is an induction period as the catalyst is reduced and then becomes active for polymerization (**Fig-1**). This catalyst is unique in that it requires no alkylating agent to generate the active species, unlike the titanium based Ziegler-Natta catalyst which also produces HDPE.

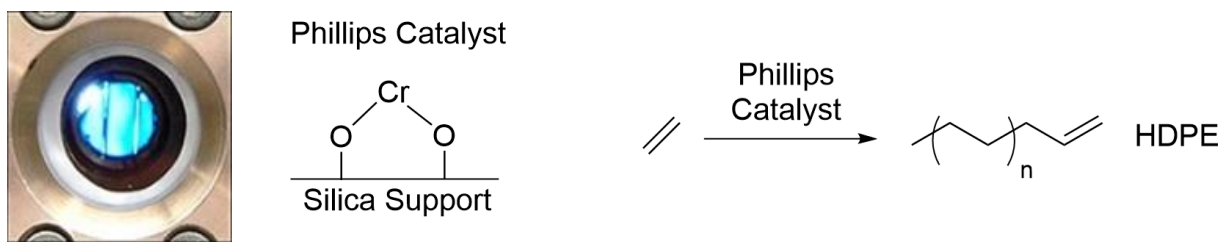


Figure 1. Proposed structure of the reduced Phillips catalyst and its use in the production of high density polyethylene

Over the past 50 years the Phillips catalyst has been studied quite extensively, but the mechanism and oxidation state remain elusive. This is due to the low number of active sites (10%), heterogeneous silica support, exceedingly fast rates and multiple oxidation states on the chromium. The mechanism of polymerization is believed to follow a Cossee Cr-alkyl mechanism (**Fig-2**).³ However, the mechanism to obtain the first Cr-alkyl species is unknown as it requires an extra hydrogen, referred to as the missing hydrogen problem. Various other mechanisms have been proposed over the years that bypass this problem including the Metallocycle⁴, Carbene⁵ and Proton Transfer⁶ mechanisms (**Fig-3**). However recent isotope studies⁷ along with DFT computations ($\omega\text{B97X-D}$, TZVP basis set)⁸ to estimate polymerization rates have shown that only the Cossee Cr-alkyl propagation mechanism is consistent with experimental studies. Its initiation mechanism still remains unknown.

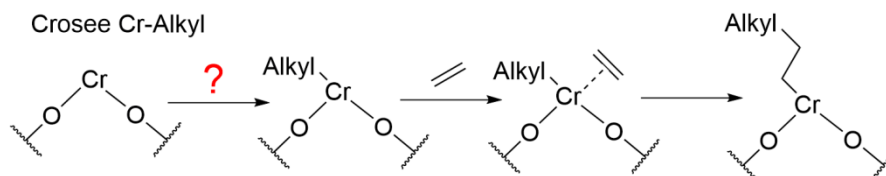


Figure 2. Cossee Cr-Alkyl mechanism for Phillips catalyst

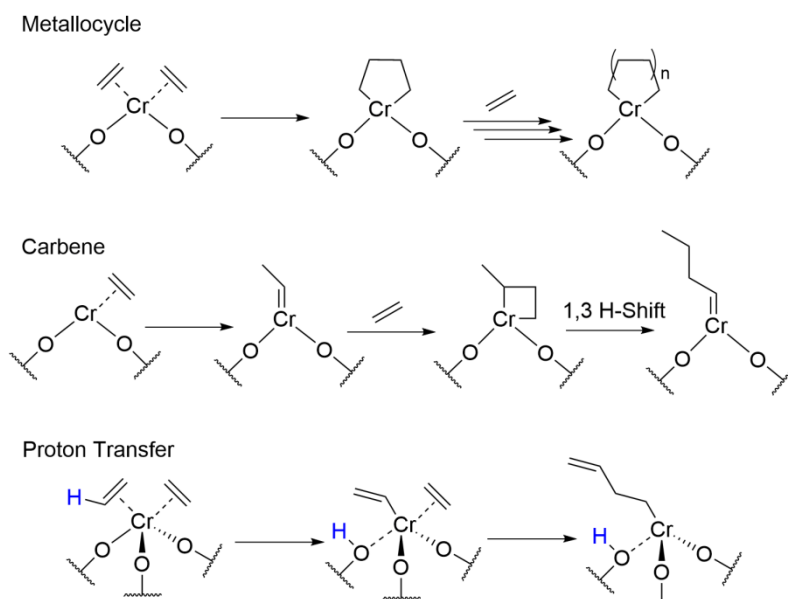


Figure 3. Mechanisms proposed that bypass the missing hydrogen problem

Besides the mechanism of the catalyst, the initial oxidation state of the chromium precatalyst before introduction of ethylene is hotly debated. While it is generally accepted that the main oxidation state of the Phillips precatalyst is +2, the low number of active sites suggest this may not be the active oxidation state. Recently two groups led by Susannah Scott and Christopher Copéret have published studies on the active oxidation state for the chromium precatalyst. Through controlled reduction coupled with characterization by X-ray absorption near edge spectroscopy (XANES) and high frequency electron paramagnetic resonance (HFEP) of the actual Phillips catalyst, Susannah has shown that the +2 oxidation state is the active precatalyst.⁹ While Christophe has shown through polymerization rates and poisoning studies of heterogeneous model complexes that the +3 oxidation state is the active precatalyst.^{6, 10}

While industry has successfully used Phillips catalyst to make HDPE for the past 60 years, research in this area is still of interest. The selective trimerization of ethylene into 1-hexene is accomplished through a homogenous chromium catalyst.¹¹ Knowledge of the Phillips catalyst mechanism would aid in the development of future catalysts for the production of terminal olefins with longer carbon chains, which can be used in the production of lubricants and other polymers such as linear low density polyethylene (LLDPE) a variant of LDPE.

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