

Ziegler-Natta Catalysis: The Nature of the Active Site

Philip D. Lane

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Karl Ziegler, while studying ethylene insertion into aluminum-alkyl bonds, serendipitously discovered the effect transition metals had on ethylene polymerization. He and Giulio Natta made significant contributions to the catalytic polymerization of olefins using a transition metal from groups 4-8 and an organometallic from groups 1, 2, or 13, the most famous combination being $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$ for the polymerization of polyethylene. The Nobel Prize in Chemistry was awarded to them in 1963 for their contributions in this area [1,2]. The importance of this catalytic process can be seen by the amount of polyethylene produced in the U.S. In 1990, 8.3 billion lbs. of high-density polyethylene were produced [3].

The heterogeneous nature of Ziegler-Natta catalysts make them difficult to study [1,4,5]. Despite improved techniques for studying surfaces, information on an atomic level about the active sites remains elusive. For example, the surface reaction of $[\text{Zr}(\text{allyl})_4]$ with SiO_2 leads to different surface species [5]. It is not clear which of the resulting surface species is responsible for the polymerization process.

Various mechanisms [6,7] have been proposed for Ziegler-Natta catalysis, with the most widely accepted proposal from Cossee and Arlman (Figure 1). The aluminum-alkyl is suggested to be responsible for alkylating the transition metal which is in an octahedral environment with one site vacant. Ethylene is thought to coordinate, followed by direct insertion into the metal-alkyl bond of the transition metal. The growing polymer then migrates back to its original position.

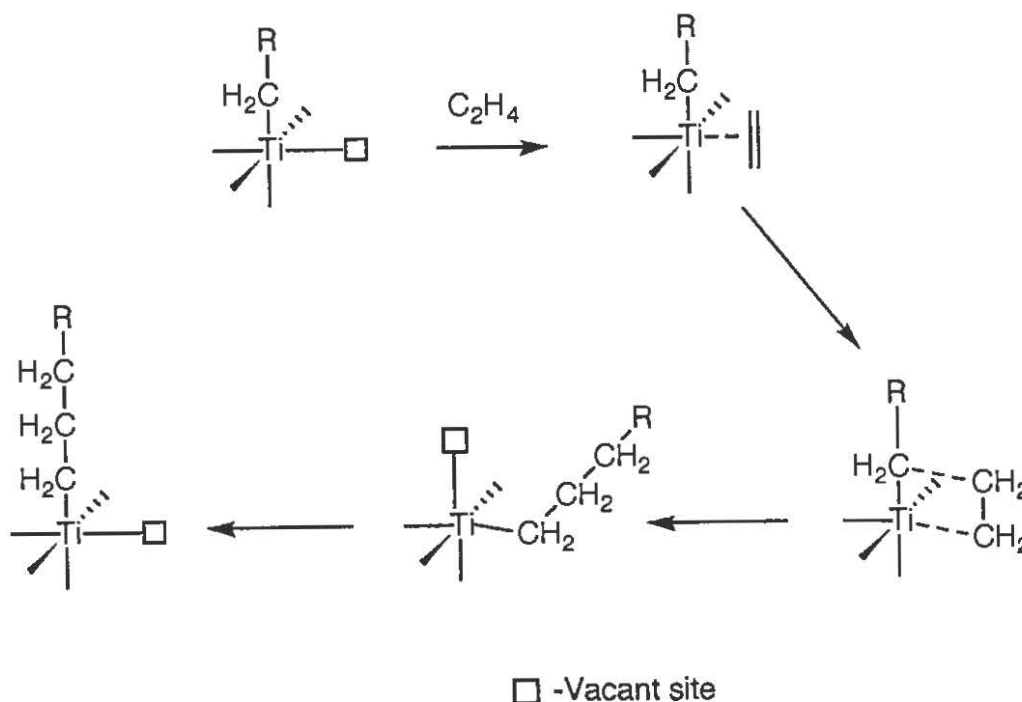


Figure 1. Cossee-Arlman direct insertion mechanism for the polymerization of polyethylene.

Evidence for this direct insertion mechanism comes from Eisch and co-workers, where direct insertion by an alkyne into the titanium-methyl bond of the reaction intermediate, $[\text{Cp}_2\text{TiCH}_3][\text{AlCl}_4]$, was observed by ^1H NMR spectroscopy and characterized by X-ray crystallography [8]. Other evidence for the transition metal being the active site is the high activity of ethylene polymerization when $[\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4]$ is supported on Al_2O_3 in the absence of an alkylating co-catalyst [5].

Due to the difficulty in studying heterogeneous systems, research has been targeted at soluble Ziegler-Natta systems. Shortly after Ziegler's discovery, Shilov and D'yachkovskii carried out experiments involving soluble zirconocene compounds [9-11]. They concluded from a series of conductivity and electro dialysis experiments that there was an ionic nature to the catalyst and proposed the species $[\text{Cp}_2\text{TiR}][\text{AlRCl}_3]$.

Considerable work has gone into the preparation and characterization of zirconocenes [13]. One of the first cationic zirconocenes, $[\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})]^+$, was not an effective catalyst for ethylene polymerization. The low activity was attributed to THF occupying the coordination site for ethylene [14]. A base-free cationic zirconocene, $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)]^+$, was identified by Jordan [15] in low temperature ^1H NMR studies, but direct interaction with ethylene could not be seen. A base-free zwitterionic complex, $[\text{Cp}^*\text{Zr}^+(m\text{-C}_6\text{H}_4)\text{B}^-\text{Ph}_3]$, was made having an activity which rivals those of the highly active alumoxane cocatalyst systems [16].

The Ziegler-Natta catalysts are still poorly understood. However, there is strong evidence for the zirconocene catalyst systems, that a d^0 , coordinatively unsaturated species is required for ethylene polymerization.

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