



Metallocene and Ziegler-Natta catalyst: a comparison

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Abstract: In this paper we are going to study the differences between a Ziegler-Natta and metallocene catalyst. Both of these catalysts differ from in each other in structural configuration, physical properties, chemical properties, activity, temperature stability etc. The purpose of this paper to study and compare metallocene catalyst with Ziegler-Natta catalysts to extract valuable aspects of both the catalysts. Catalysts can impact the rate of formation of polymers within the metallocene polymerization.

Keywords: Metallocene Catalysts, Ziegler-Natta Catalyst, Temperature

1. Introduction

Polymers are the most abundant class of polymers which are synthesized using both metallocene and Ziegler-Natta catalyst (Chung et al., 2002). When metallocene catalyst were introduced it was believed they will bring a revolution in the polymer industry but till date only 5% polyolefin is synthesized using metallocene catalyst. In the products having high density there is no significant difference between metallocene and Ziegler-Natta catalyst (SL Shenoy, 2005).

In the low-density ethylene elastomer market metallocene catalyst have made a great impact. 42% of global ethylene elastomer is synthesized using metallocene catalyst (Credendino et al., 2015). Metallocene differentiate themselves from Ziegler Natta catalysts at low density (Zakharov et al., 2008).

2. General catalyst comparison

2.1 Structure

Ziegler-Natta catalyst are formed with a combination of metallic halides and it's co-catalyst. They form coordination complexes with multiple active sites (Parvez et al., 2014). These catalyst produce products with broader distribution of chains so there is variation in distribution of properties. Modifiers can be added to Z-N catalyst to reduce the multi-site nature of such catalysts (Matsko et al., 2009).

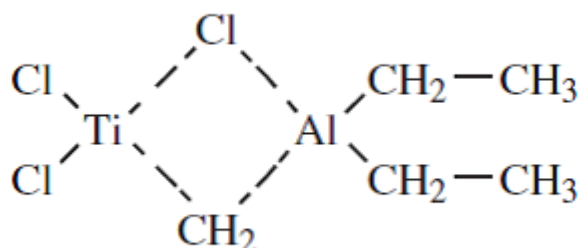


Figure 1: Structure of a Ziegler-Natta catalyst

Metallocene (Zohuri et al., 2012) comprises of a very well formed chemical structure composition which can be separated by using X-ray crystallography mechanism. Such catalysts operate on one active site which works on a uniform ligand environment thus narrow distribution of properties takes place (Resconi et al., 2000). One can alter the application of it's products by modifying the structure of metallocene catalyst.

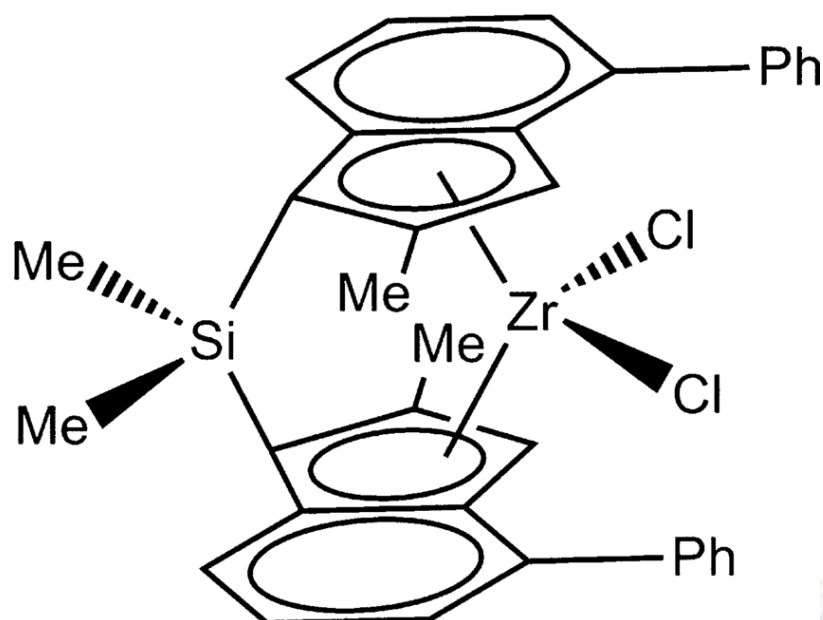


Figure 2: Structure of a metallocene catalyst

2.2 Temperature stability

Ziegler Natta catalysts in general cannot resist high temperatures. As the bonding between chemical complexes is loose these catalyst lose a huge amount of their chemical activity even at a temperature of 60°C.

On the other hand metallocene have great temperature stability and remains active even at temperature 200°C. These catalyst have high temperature bearing capability which allows them to have a great range of composition.

2.3 Comonomer Incorporation

Higher olefins are poorly catalyzed by Ziegler-Natta catalyst. Rate constants for higher polymerization olefin drop because of being catalyzed by Ziegler-Natta catalyst (Ziegler, 2004).

Metallocene catalyst are used to easily polymerize higher alpha olefins. A great range of polymers can be polymerized using metallocene catalysts. Even elastomers like butene, hexene, and octene can be polymerized using metallocene catalyst.

2.4 Activity

For higher polymers like ethylene and propylene the activity of Ziegler-Natta reduces. Since Z-N catalyst have low activity after their reaction they leave a good quantity residue behind and de-dashing procedure is carried out to remove residue.

Metallocene catalyst have high activity and after their reaction they do not leave residue in high quantity so no de dashing procedure is required.

2.5 Branching control

Elastomers have soft and little crystal like structure.. Their melt properties arise from the entanglements of chains. These elements have high elastic and rigid properties. Processing these chains become even more difficult as elastic nature increases. There has to be a balance between properties and material to process such elastomers.

Metallocenes are different from Ziegler-Natta catalysts as they are able to sustain through a process called [beta]-hydride elimination. Elimination of hydrides forms unsaturated chain ends that can be fitted into propagating chains, forming a big chain. LCB has a dramatic influence on the rheology of the chain by reducing its coil dimensions for a given molecular weight. Low levels of LCB can often improve processing by shear thinning at high shear rates, yet maintain tensile properties at low shear rates. Since metallocenes make products with terminal unsaturation, it is possible to find conditions that influence the level of LCB and thereby to make easier processing grades (Kulkarni et al., 2014).

2.6 Stereo-regularity

Z-N catalysts and metallocenes are each capable of making stereoregular isotactic polypropylene. But it took an understanding of the well-defined catalyst structure in metallocenes to really sort out the mechanism of stereoregular polymerization. The relationship between metallocene symmetry, comonomer orientation during insertion and chain architecture is well documented. Metallocenes have been designed that enchain prochiral monomers like propylene in atactic, isotactic, syndiotactic and hemi-isotactic orientations. Even though each is homo-polypropylene, their properties are vastly different. The orientation of the



monomers has a huge effect on coil dimensions, crystallinity, viscosity, compatibility, entanglement and almost every other aspect of polymer physics (Smith et al., 2016).

Although stereoregular polymers are generally thought of as homopolymers like polypropylene, the short comonomer runs found in ethylene copolymers are still stereoregular. Three ethylene-propylene (EP) copolymers with similar composition, about 65 wt. % ethylene, were made using an isospecific metallocene, a syndiospecific metallocene and an aspecific vanadium Z-N catalyst. NMR showed that the isospecific metallocene product contained meso propylene diads, the syndiospecific metallocene product had only rac propylene diads and the Z-N product had a few random propylene dyads (Falivene et al., 2015).

3. Conclusion

Metallocenes have brought revolution in the polymerization industry and have helped in its tremendous growth. Metallocenes are being widely used in the polymerization of low-density.

Ziegler-Natta catalyst are formed with a combination of metallic halides and its co-catalyst. Metallocene comprises of a very well formed chemical structure composition.

Metallocenes can easily polymerize high olefins whereas Z-N catalyst cant. Z-N catalyst does not have a great temperature stability and metallocenes can easily resist high temperatures. If we compare chemical activity metallocenes are highly reactive and Z-N catalyst are not chemically high reactive substances. Overall we can conclude for low density substances metallocene catalyst have an upper hand over Z-N catalyst.

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