Metalloocene Catalysts for Ethylene Polymerization

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ABSTRACT

Metallocone catalysts are the latest addition to the olefin polymerization catalyst family. It has been demonstrated that metallocone catalyst can polymerize olefins at high activities. Some chiral metallocones are also capable of stereospecific polymerization where isotactic and syndiotactic polymers can be produced.

Although it was proven that metallocone catalysts can polymerize ethylene in the late fifties, it took more than 20 years before technology was developed that could provide an economically viable catalyst. In mid-eighties, Kaminsky and Sinn developed methylaluminoxane based cocatalysts that substantially increased the activity of the metallocone catalysts. After this breakthrough, many academics and most of the industrial polyolefin research organizations began focusing on the metallocone catalysts.

It is estimated that billions of dollars have already been invested in the metallocone catalyst research. Why were the industrial research organizations willing to invest such a huge amount in this research? Why did the industrial research focus on the metallocone catalyst research? This paper will address some of the major reasons why metallocone catalyst research is given high priority.

INTRODUCTION:

In the thirties, Imperial Chemical Industries (ICI) started producing polyethylene through high pressure, radical polymerization of ethylene[1]. With the invention of the so-called “Phillips-catalyst” (chromium oxide on silica gel), Hogan and Banks[2] achieved the commercial production of polyethylene at low pressure. Even today, 40% of the worldwide polyethylene production uses this catalyst[3]. Almost simultaneously, Ziegler[4,5] and Natta[6,7] discovered the catalytic activity of titanium halides in presence of aluminum alkyls for olefin polymerization at low pressure.

Up to now, the structure and functioning of polymerization active centers of these catalyst systems are not completely elucidated and understood. It is assumed that different catalyst species produce polymers with various molecular weight distribution. Polymers with defined structure became available with the discovery by Breslow and Newburg[8], and Natta[9]: metallocene (titanocene) in combination with aluminum alkyl halides can be used as homogeneous catalyst system to polymerize ethylene. However, industrial application was not worthwhile due to low activity.

The discovery of methylaluminoxane (MAO) as cocatalyst by Sinn and Kaminsky[10] in 1980 marked the most significant breakthrough in the field of metallocone catalysis. The activity of the metallocone dichloride complexes of titanium, zirconium and hafnium could be increased by orders of magnitude through the use of this new cocatalyst.
WHAT ARE METALLOCENES:

Metallocene compounds are discrete molecules that have two cyclic ligands bonded to a metal center [Figure 1]. In the industrial environment, the term metallocene is often used for all single-site catalysts. A wide variety of metallocenes are used for olefin polymerization today.

METALLOCENE CATALYSTS:

Metallocenes by themselves are not active for polymerization. Usually, a cocatalyst is required to activate the metallocene. Methylaluminoxane(MAO) or borate compounds are used to activate the metallocene\(^{[11]}\). MAO methylates the metallocene dichloride complex and then abstracts one methyl anion to produce a metallocene monomethyl complex. Therefore, the metallocene monomethyl cation produced is considered as the catalytically active species\(^{[12,13]}\) [Figure 2]. The activated metallocene catalysts can be used for olefin polymerization.

There are three different commercial olefin polymerization processes where metallocene catalysts can be used. They are the: Solution, Gas phase and Slurry process. Homogeneous or heterogeneous catalysts are used in the Solution process. Metallocene catalysts are inherently soluble catalysts (homogeneous). Therefore, the Solution process was the first commercial process to use metallocene catalyst to produce polyethylenes. Gas phase and Slurry process require heterogeneous catalyst. Metallocene catalysts need to be supported so that they can be employed in Gas phase or Slurry phase olefin polymerization processes. They can be supported in three different ways: 1) The metallocene compound is reacted with supported MAO to produce a supported catalyst. 2) The next option is to react a cross-linked MAO, which is insoluble in hydrocarbon, with a metallocene compound to produce a supported catalyst. The cross-linked MAO may or may not contain inert supports. 3) The third option is to support the metallocene compound and react it with soluble MAO.

WHAT IS SPECIAL ABOUT METALLOCENE CATALYSTS:

It is estimated that billions of dollars have already been invested in the metallocene catalyst research. Why were so many industrial research organizations willing to invest such a huge amount in this research? Why did the industrial research focus on the metallocene catalyst research?

Some of main factors that influenced the research spending in this area are: 1) high productivity of the catalyst; 2) Narrow molecular weight distribution (MWD); 3) Better comonomer distribution; 4) Better tailoring of the resin.

Metallocene catalysts have in general demonstrated high productivity. H.G. Alt et al. published\(^{[14]}\) activity for bisfluorenyl to be as high as 60,000,000 gPE/g metal. Higher productivities for catalysts translate to lower catalyst cost and cleaner polymer. A comparison of the PE produced with metallocene, Ziegler-Natta and chromium catalysts is shown in Figure 3. PE produced with metallocene catalysts have narrower MWD than the polymers produced with the other two catalyst systems. The comparison was made for one MI polymers. Metallocene polymer has less low-molecular weight material than other polymers. This reduces the smoke, taste and other process difficulties associated with low molecular weight polymers. On the other side, polymers with narrow molecular weight distribution are usually difficult to process in existing equipment. One of the
reasons why metallocene resins have better properties than Ziegler-Natta and chromium resins is due to the fact that they have higher amount of high molecular weight fraction. A comparison of the comonomer efficiency of the three catalyst systems is shown in Figure 4. The metallocene catalysts have greater efficiency in using comonomer to reduce the density. In other words, Metallocene catalysts require less comonomer to achieve the same density and that in turn reduces the production cost of the low-density polymer. This is one of the reasons why all the companies involved in the metallocene catalysis introduced low-density polymer first to the market. Yet another advantage of metallocene resins is the ability to tailor the resin. Metallocene catalysts are capable of producing polymer with varying molecular weight and comonomer incorporation. Combining various metallocenes in one reactor can produce high performance bi-modal resins with molecular weight and comonomer segregation. One such example would be a combination of unbridged bispentadienyl metallocene with bridged bisfluorenyl metallocene. Unbridged bispentadienyl metallocene would produce low molecular weight homopolymer and the bridged bisfluorenyl metallocene would produce high molecular weight copolymer. For mono-modal polymers the processing and properties goes in the opposite direction. The above bi-modal polymer form metallocene will have better processing through molecular weight segregation and better properties through comonomer segregation. The metallocene catalyst technology will enable to materialize a long dream of the polyolefin industry – develop a polymer with superb processing and properties. Last but not least the metallocene catalysts are capable of producing homo and copolymers that were economically unfeasible before. Polymers and copolymers of cyclic olefins are good examples of such polymers. Unfortunately due the unclear patent situation, most of the companies are holding back on introducing new products to the market. As it is the case with any new technology, it will take 10 – 15 years before large-scale market introduction materializes.

CONCLUSION:
Metallocenes will revolutionize the polyolefin industry by opening new opportunities that were not accessible in the past. Major polyolefin producers will need a strong metallocene program to be able to compete in the future.

REFERENCES:

Figures:

**Figure 1: Types of Metallocene used for Ethylene Polymerization**

- Cyclopentadienyl, Indenyl, Fluorenyl (Substituted & Unsubstituted)
- \( M = Ti, Zr, Hf \)
- \( B = \text{Bridge} \)
Figure 2: Activation of Metallocene with MAO
Figure 3: Comparison of MWD’s of different PE’s

![Figure 3: Comparison of MWD’s of different PE’s](image)

Figure 4: Comparison of comonomer efficiency of different catalysts

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