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PAST AND FUTURE PERSPECTIVE OF METALLOCENE CATALYST: A Review

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Abstract: In the mid of 1980 there has been a revolutionary development in the catalyst technology after the discovery of metallocene catalysts. Group 4 metallocenes and constrained geometry catalysts have been at the fore front of the developments. In the late 1990, these catalysts are growing in commercial operations. Metallocene and other transition metal complexes plays an important role as highly active catalysts for the polymerization of polymers especially polyolefins, styrene etc. Experimental studies on different parameters like catalyst activity, effects of operating conditions, cocatalysts etc. have been studied by the researchers. In this review, the past, present and future scenario of metallocene catalysts is highlighted.

Keywords - Metallocene, polyolefins, styrene, active catalyst

1. INTRODUCTION

Metallocene catalysts are metal complexes with two cyclo penta dienyl (Cp) or substituted Cp groups. Standard Ziegler-Natta catalysts, in contrast, are typically built from titanium and chlorine.

Metallocene catalysts are homogeneous single-site systems, implying that a single catalyst is present in the solution. In contrast, Ziegler-Natta heterogeneous catalysts probably contain a distribution of catalytic sites. The catalytic properties of single-site catalysts can be controlled by modification of the structure of the ligand. A post-metallocene catalyst, a class of homogeneous catalysts and a kind of catalyst for olefin polymerization has attracted much attention, although traditional heterogeneous Ziegler-Natta catalysts still dominate the industry. The use of metallocene catalysts in the production of PP homopolymers results in resins with improved optical and processing characteristics, combined with exceptional purity.

Metallocene dihalides [Cp_2MX_2] (M = Ti, Mo, Nb) exhibit anti-tumor properties, although none have proceeded far in clinical trials.[12] Many derivatives of early metal metallocenes are active catalysts for olefin polymerization. Unlike traditional and still dominant heterogeneous Ziegler-Natta catalysts, metallocene catalysts are homogeneous.

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2.PAST AND PRESENT ACTIVITIES

Chemists had been aware of metallocene structures since the 1950s. But their commercial utility didn't become apparent until 1977, when Walter Kaminsky at the University of Hamburg demonstrated that metallocenes, with the help of a methyl aluminoxane cocatalyst, could be useful in polymerizing olefins.

Dozens of chemical companies raced to develop an ever-increasing number of catalyst structures, yielding an enormous stable of new materials. The foundational R&D work reached a crescendo in 2002. According to Science IP, the patent search arm of Chemical Abstracts Service, the number of patents published for metallocene polyolefin catalysts peaked that year at 387 globally.

Still, by 2004, there were more than enough new resins on the market that the industry could turn to application development. "The fabricators and the processors started dealing with qualifying these resins," said John J. Murphy, president of Catalyst Group Resources. The researchers were determining whether the resins were in fact necessary for the applications and the degree to which they should be substituted for traditional Ziegler-Natta-based materials.

In 2009, 5 million tons of metallocene LLDPE was consumed nearly 25% of the global LLDPE market, according to Murphy. "Growth rates for metallocene resins were high single digits as opposed to traditional resins, which had witnessed reduced growth patterns over the last couple of years," Murphy said. Also, LLDPE and HDPE together amount to another 3 million tons of metallocene resin demand, Murphy said.

Metallocene resins established as a hard-fought battle in the LLDPE market in the mid-1990s had strong properties to offer converters, said Steven F. Stanley. "The big improvement in the dart impact over conventional resins was one of the clear areas where metallocene resins had delivered on what was hyped," Stanley says.

STA Research's Sinclair said that thousands of processors were forced to blend LDPE with the metallocene-based LLDPE as LDPE was more expensive than Ziegler-Natta LLDPE and using it diluted the metallocene LLDPE's exceptional properties.

F. Gregory Stakem, vice president of technology at Univation, recalls "In the beginning, people thought metallocenes would penetrate a lot quicker than they did," He compared the situation to the 1980s, when LLDPE, then in its infancy, would supposedly spell the end of LDPE made in high-pressure reactors. "LDPE is bumping along with 2% growth rates every year."

However, the plastics industry has been chipping away at metallocene-resin-processing problems, Stakem says. Converters have modernized their equipment, and resin companies have come out with new products and developed new applications. Machinery for multilayer film has taken off in recent years. This technology allows metallocene resins to be layered with cheaper, conventional LLDPE. The thinner gauge of the film is also easier to process.

ExxonMobil introduced its Enable line of metallocene polyethylenes in 2008, which were meant to do the work of LDPE/metallocene LLDPE blends in a single resin. The company

boasts that Enable could increased output by 20% versus the older blends. Theodore J. Wojnar Jr., senior vice president of ExxonMobil Chemical, said that metallocene are growing much faster than overall polyethylene is growing."

Total Petrochemicals introduced a new generation of metallocene polyethylenes and polypropylenes under the Lumicene tradename. The product line includes next-generation medium-density polyethylene (MDPE) grades for easy processing.

In contrast to their success in polyethylene, metallocene catalysts have struggled to capture much of the polypropylene market. About 1.4 million metric tons of metallocene polypropylene was purchased last year, according to Catalyst Group Resources' Murphy, representing only about 2 to 3% of the world's polypropylene demand.

In addition, STA Research's Sinclair said metallocene catalysts had more difficulty overcoming their limitations with polypropylene as propylene polymerization yields a lot of by-product hydrogen when it is catalyzed with metallocenes. Hydrogen terminated

the polymerization prematurely, leading to low-molecular-weight polymers with viscosity that is too low for many applications.

However, Mike Musgrave, market manager for molded applications at Total Petrochemicals USA, says new Lumicene metallocene polypropylenes have lower melt flow than earlier metallocene polypropylenes. This has helped open up blow molding and thermoforming applications, such as disposable drinking cups to metallocene polypropylene. In that market, metallocene polypropylene has clarity and gloss advantages that allow polypropylene to compete with polyethylene terephthalate.

In 2008, Albemarle, which supplies catalysts and MAO activators to polymer companies, launched its ActivCat activator technology based on MAO-type technology which is double catalyst activity without adversely influencing resin properties. The activators can help bring down the cost of metallocene catalysts for polypropylene as well.

New, cost-effective activators have spurred metallocene resin demand, Motto says. "It took a while to develop, but now metallocene catalysts are on a sustainable growth path," says Anthony J. Dondero, vice president and general manager of specialty catalysts and process technologies at Grace Davison.

Another sign the metallocene catalyst industry is building steam is that resin developers are once again adventurous in introducing new platforms, many outside their comfort zone of LLDPE for film.

3. FUTURE PROSPECTIVE

The metallocene approach has matured significantly in the last years, small production with higher prices to an increasing factor in the polymer industries. Investigations have not been ended up to now in tis fascinating research areas.

Univation's Stanley believes the market penetration of metallocene polyethylene will double by 2020, largely because of emerging opportunities in HDPE, in addition to growth in LLDPE.

The original focus for the new catalysts was to improve the tear-resistance of metallocene LLDPE film. Since then, Univation has been applying the XCAT VP catalysts to HDPE, particularly in injection- and rotational-molding applications.

Multisit catalysts are used to bring reduced cycle times and strength for fabricating plastic parts and metallocene catalysts for making bimodal HDPE, used in pipe fabrication, in a single reactor Stakem says.

Like all new products, the resins will enter into the long application development phase. The industry may have overestimated the time and effort to introduce new metallocene resins in the past, but it isn't likely to again. Having seen this process play out before, Stakem is prepared. "The resin market is big, and it is really hard to turn a big boat," he says.

Now, more active catalysts and adapted processes have to be developed for the evolution of new polyolefins showing unique properties with incorporation of new co- monomers or by adopting new strategies.

Today, millions of tons of metallocene resins are made every year, and they enjoy more robust growth than traditional plastics.

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