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Nickel and Palladium Catalyzed Olefin Polymerization

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Abstract

This review summarized the progress on transition metal catalysts for olefin polymerization, and focuses on the olefin polymerization by the late transition metal catalysts and the recent advances in catalyst design. In recent years, nickel and palladium complexes for olefin polymerization have received extensive researches owing to the precise control of branching microstructure, molecular weights and properties of the resulting polyolefins.

Keywords: Nickel and palladium complexes; Olefin polymerization; Chain-walking; Branched polymer

Abbrevations: MAO: Methylaluminoxane; CGC: Constrained Geometry Catalysts; LDPE: Low Density Polyethylene; LLDP: Linear Low-Density Polyethylene; HDPE: High-Density Polyethylene; PP: Polypropylene

Introduction

The research of the ethylene and α-olefins polymerizations using late transition metal catalysts should be highlighted for development of polyolefin materials during the past two decades [1-5], because polyolefin materials are tremendously important in daily life [6]. Branched polyolefins are generally produced by transition-metal catalyzed copolymerization. The physical properties of polyolefin materials can be dramatically affected by their microstructures, which are controlled by the catalyst structures and their catalytic behavior. Progress of molecular the catalysts of transition metal complexes during these three decades enabled control of stereochemistry of poly(α-olefin)s, control of molecular weight of polyethylene and poly(α-olefin) s, synthesis of block copolymers by living polymerization, and copolymerization with various comonomers including polar functionalized olefins [5]. Thus, the design and synthesis of novel transition metal catalyst has always been a research focus of the polyolefin research.

In 1950s, Ziegler & Natta discovered that the mixture of titanium chloride and alkyl aluminum compounds enabled polymerization of ethylene and propylene, the synthesis of High Density Polyethylene (HDPE) and isotactic polypropylene, respectively. The discovery of [7] catalysts (Figure 1) not only revolutionized polyolefin production, but also catalyzed the development of the entire organometallic chemistry field.

In 1980s, Kaminsky [8] discovered that Methyl Aluminoxane (MAO) as an excellent co-catalyst to highly activate half-metallocene's [8] and badged metallocene catalysts for alkene polymerization to produce polymers of narrow molecular weight distribution. The second milestone in alkene polymerization catalysis was the development of metallocene catalysts.

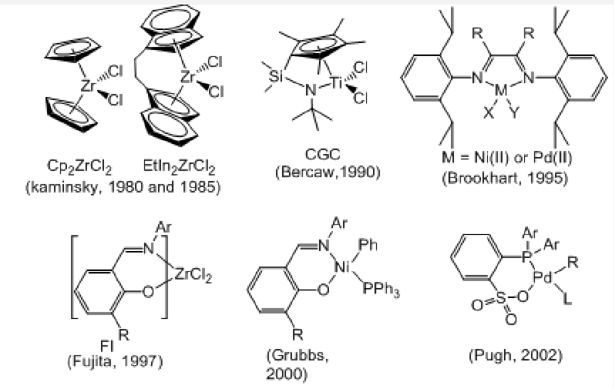

Figure 1: The typical structure of transition metal catalysts for olefin polymerization.

In 1990s, Bwren reported that the constrained geometry catalysts (CGC, Figure 1) [9] exhibited their unique properties in the catalysis and revealed the relationship between the structure of the catalysts and stereoselectivity of the reaction, and showed high activity for ethylene and 1-alkene copolymerization. In addition, Fujita also reported that the bis(imine-phenoxy) titanium and zirconium complexes (FI catalysts, Figure 1) exhibited high activity for ethylene polymerization [10].

In 1995, Brookhart [11] discovered that nickel and palladium complexes with bulky diimine ligands showed high catalytic activity for ethylene and α-olefin polymerizations [11] to produce high molecular weight polyethylene with different polymer topologies and branched poly(α-olefin)s [12-13]. Interestingly, these nickel and palladium catalysts are also used for copolymerization of ethylene with polar monomers to afford the copolymers possessing functional groups in a single step because of their good tolerance toward polar functionality [14,15].

The discovery of late transition metal nickel and palladium catalysts has initiated a new olefin polymerization field. In 1998, Gibson [16] and Brookhart [17,18] reported that Fe and Co catalysts with bis (imino) pyridine catalyzed ethylene polymerization efficiently to afford linear polyethylene. In 2000, Grubbs [19] reported that neutral nickel catalysts [19] containing salicylaldimine ligand are used for polymerization of ethylene. In 2002, Pugh [20] reported that palladium catalysts with phoshine sulfonate ligand can produce unique polymers such as a highly linear copolymer of ethylene and alkyl acrylates [20] and a non-perfectly alternating copolymer of ethylene and CO [21].

In this review, recent progress on late transition metal catalysts for ethylene or α-olefin polymerizations are summarized [1]. Systematical study elucidated the effects of late transition metal ion, α-diimine backbone and the ligand on it, the effects of polymerization conditions (temperature and pressure) on the catalyst's performance, branching degree, molecular weight and its distribution of the polymer and the properties of the polymer produces.

Chain-walking ethylene polymerization by nickel and palladium catalysts

The research of the ethylene polymerization catalyzed by late transition metal catalyst should be highlight for development of polyolefin materials in recent years [22-28], because polyethylene is probably the polymer you see most in daily life. There are three main types of polyethylene namely: Low Density Polyethylene (LDPE), Linear Low-Density Polyethylene (LLDP) and High-Density Polyethylene (HDPE).

Chain-walking ethylene polymerization mechanism

The discovery of nickel and palladium α-diimine catalysts (Figure 2) by Brookhart et al. [11] in the 1990s is another further major advance in the alkene polymerization catalysis [11-13]. Distinctly different from other catalysts, this unique series of late transition metal catalysts is featured with their characteristic chain-walking mechanism and allow the unprecedented one-step synthesis of polyethylenes with controllable chain topology [29-33].

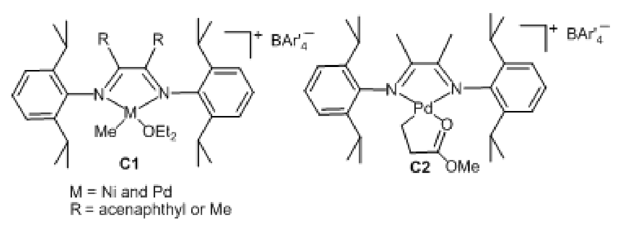

Figure 2: Brookhart's catalysts for olefin polymerization.

The nickel and palladium α-diimine catalysts C1 and C2 (Figure 2) showed high activity for polymerization to produce different branched polymers, depending on the catalyst structures and the polymerization conditions (temperature and ethylene pressure), because the the ability of the propagating metal-alkyl species to migrate along the growing polymer chain via rapid β-hydride elimination and reinsertion (chain-walking, (Figure 2) [34-37]. The formation of the major types of branches including the methyl, ethyl, propyl, butyl, sec-butyl and longer chains, in the branched polyethylene [36,38]. The mechanism of chain-walking for ethylene polymerization is shown in (Figure 3).

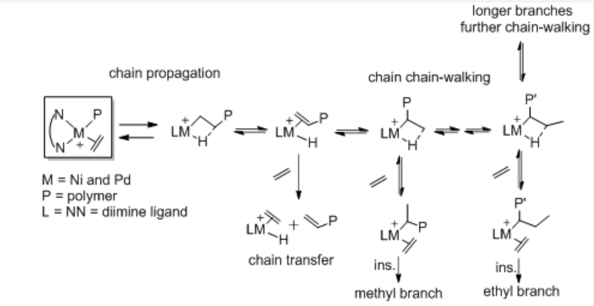

Figure 3: Chain-walking mechanism for ethylene polymerization with α-diimine nickel and palladium catalysts.

The degree of the polyethylene branching can be controlled via polymerization conditions [1,39] as follows. For example, Guan et al. [40,41] demonstrated that ethylene pressure has been used to control the competition between monomer insertion and chain-walking processes for ethylene coordination polymerization catalyzed by a palladium α-diimine catalyst C2. The topology of the polyethylene changed from linear polyethylene with moderate branches at high ethylene pressures to a hyperbranched polyethylene at low pressures.

Modified nickel and palladium catalysts

Previous studies showed that sterically bulky ligands are usually required to afford nickel and palladium catalysts capable of generating high activity, stability and high molecular-weight polymers [42-48]. Besides, linear polyethylene via chain straightening mechanism is the most abundantly produced plastic owing to its inexpensive monomer, thermoplastic properties, and semi-crystalline nature [1]. The degree of the polyethylene branching can be controlled via catalyst structures and polymerization conditions. For example, Schmid et al. [49] reported a new "Ortho-Aryl Esffect" using terphenyl substituted 1,4-diaza-

1,3-butadiene ligands: the corresponding nickel complexes C3 were highly active catalysts for ethylene homopolymerization to produce almost perfectly linear polyethylene's in the presence of hydrogen [49].

Guan et al. [50-52] designed the macrocyclic ligand by connecting the aryl substituents of 2,6-diarylphenylimino moieties using ethylene tether. Their cyclophane-based nickel and palladium catalysts C4 showed significantly higher thermal stability than the acyclic analogs [49-52]. The palladium catalysts also generated polymers with significantly high branching density compared to the acyclic counterparts, suggesting faster chain-walking process [50]. The cyclophane-based nickel catalyst promoted living polymerization of propylene even at 50–75°C [51]. This type of catalyst enhances both the 2,1-insertion of propylene and the chain-walking reaction. The branching density of the generated Polypropylene (PP) is slightly above 100/1000C, which is only half of the value comparing with conventional α-diimine nickel catalyst. Besides, the palladium catalyst incorporated a much higher amount of Methyl Acrylate (MA) than the acyclic analogue (Figure 4).

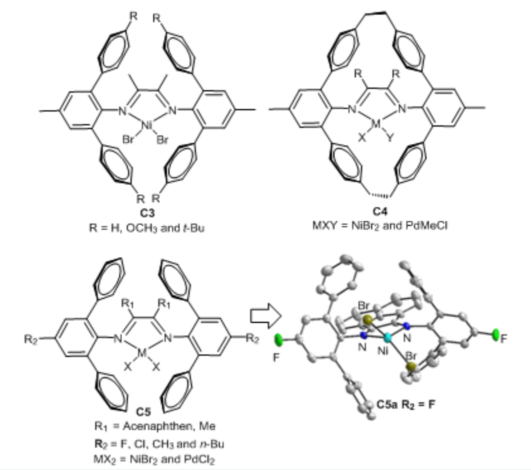

Figure 4: Structure of ortho-teraryl-substituted α-diimine nickel and palladium complexes.

Inspired by these works, we recently reported a series of α-diimine nickel and palladium complexes C5 [53,54] containing 2,6-diphenyl groups. These nickel complexes exhibited high catalytic activity in the polymerization of ethylene (up to 106g PE/(mol Ni h bar)) and produced highly-branched polyethylenes at high temperature upon activation with Et2AlCl. The introduction of an electron-withdrawing group to the ligand framework improves the catalytic activity significantly. We also reported a series of α-diimine nickel complexes [35,37,42] containing para-phenyl or para-naphthyl substituents for ethylene polymerization under low ethylene pressure. These nickel complexes also exhibited high catalytic activity and produced highly-branched polyethylenes.

Brookhart et al. [55] reported a "sandwich" α-diimine nickel catalyst C6a incorporating two 8-p-tolylnaphthylimino groups which provide exceptional shielding of the two axial sites were shown to produce highly branched polyethylene (up to 152 branches/1000C) [55] with ultra-high-molecular-weight. Recently, they also studied a "sandwich"-type diimine palladium catalyst C6b for ethylene polymerization, the catalyst conducted living polymerization at 25°C and produced hyperbranched polymers [56] (Figure 5).

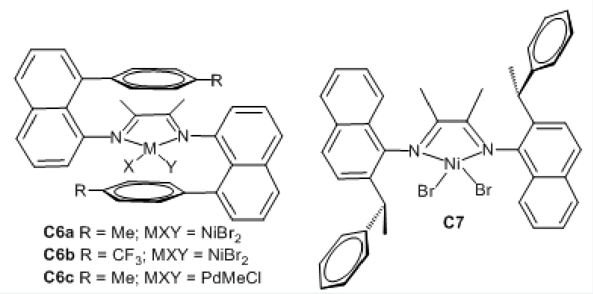

Figure 5: Structure of naphthyl-α-diimine nickel complexes.

Coates et al. reported that the precision chain-walking polymerization of higher α-olefins using the "sandwich" α-diimine nickel catalyst C6c [57] and some derivative catalysts to afford highly "chain-straightened" semicrystalline polymers (Tm > 100°C) with a significant fraction of 1, ω-enchainments. We have reported that a similar naphthyl-α-diimine nickel catalyst C7 bearing chiral bulky sec-phenethyl groups in the o-naphthyl position, activated by Et2AlCl [58], showed highly catalytic activity for the polymerization of ethylene (2.81 × 106 g PE (mol Ni h bar) −1) and produced branched polyethylene. Interestingly, C7 could Produce Syndiotactic PMMA at low temperature (rr up to 88.75%, -30°C).

Conclusion

In this review, the progress on transition metal catalysts for olefin polymerization were summarized. We first briefly discussed the chain walking mechanism of nickel and palladium catalysts in ethylene polymerization. Subsequently, some recent advances in the α-diimine-based nickel and palladium catalysts development were summarized. Specifically, the modifications on N-aryl substituents were described.

Acknowledgements

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