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Review

Catalytic and coordination facets of single-site non-metallocene organometallic catalysts with N-heterocyclic scaffolds employed in olefin polymerization

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ABSTRACT

This review discusses the principles underlying mononucleating N-heterocyclic ligand design, selectivity of metal centers, preparation of organometallic catalysts with a N-heterocyclic backbone, and their catalytic activity in olefin oligo/polymerization. A vast number of N-heterocyclic organometallic compounds have been applied for the polymerization on account of their modest cost, low toxicity, and the large availability of transition metals in stable and variable oxidation states, which makes them versatile precursors for these reactions. The main points of focus in this review are the key advances made over more the past 25 years in the design and development of non-metallocene single-site organometallic catalysts bearing different N-heterocyclic scaffolds as a backbone. These catalysts are applied as precursors for the transformation of ethylene, higher α-olefins, and cyclic olefins into oligo/polymers. Emphasis is placed on the architecture of ligand peripheries for tuning the formed polymer properties and the consequences on product formation of different alkyl or aryl substituents directly attached to the metal center in a N-heterocyclic ligand system.

1. Introduction

The crucial properties of organometallic catalysts for olefin oligo/polymerization include the nature of the metal ions and the three-dimensional orientation of the ligands and positions of suitable alkyl or aryl substituents. This understanding has motivated the synthesis of novel mono-, bi-, and polynuclear organometallic catalysts for the production of desired polyolefins [1–3]. Non-metallocene organometallic catalysts encompassing N-heterocyclic scaffolds are employed in the hope that similar synergistic effects will occur as in metallocene-based catalysts, where the metal center is directly linked to an aromatic ring system. In this stream, many organic aromatic N-heterocycles have been employed as backbone synthons in ligand design with defined sub-

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stituents at appropriate positions on the heterocycles [4,5]. Very few articles are available in the literature on organometallic binuclear catalysts designed specifically for olefin oligo/polymerization, in which both metal centers are separated by a bridging unit present in the heterocycle or by aliphatic/aromatic spacers. A variety of N-heterocycles can be exploited in the design of ligands for olefin oligo/polymerization because of their potential chelating properties towards electropositive metal atoms/ions to form stable catalysts. Very recently, non-metallocene single-site late transition metal catalysts have attracted attention in studies on the implications of electronic and steric effects originating from ligands on the oligo/polymerization of olefins [6]. Recent studies in this area using N-heterocycles such as pyridazine, pyrazole, and pyridine have encountered diverse and difficult challenges. Pyridine, acridine, pyrrole, and phenanthroline have been extensively studied for use in monometallic catalysts and pyrazole, pyridazine, and phthalazine, for bimetallic catalysts for olefin oligo/polymerization, with various substituents. These heterocyclic compounds are an important class of nitrogen heterocycles characterized by one or two nitrogen heteroatoms in an unsubstituted parent compound. The lone pair electron on the heteroatom may not be involved in the delocalization into the aromatic pi-electron system; hence, it acts as an organic base with properties similar to tertiary amines. Nitrogen heterocycles can undergo protonation, alkylation, acylation, and N-oxidation at the heteroatom like tertiary amines because of their basic character. The heteroatom is more electronegative in nature and has a strong tendency to donate the electron lone-pair to electropositive organometallic precursors under appropriate reaction conditions to form stable coordination compounds or complexes. The extent of nitrogen denticity depends on the nature and position of substituents on the heterocyclic ring system as well as the nature of the accepting atom/ion. For instance, in pyridine, electron-withdrawing groups at the *ortho*- and/or *para*-positions affect chelation by increasing the chance of back-bonding rather than the usual nitrogen lone-pair coordination. Conversely, electron-donating groups at the said positions enhance chelation from nitrogen and form stable coordination compounds of the desired compositions. However, the effect of substituents at the *meta*-positions is opposite to that at the *ortho*- and *para*-positions. These substituents are responsible for obtaining definite electronic and steric modulations in the ligand systems, which is a major consequence in getting the desired oligo/polymer in olefin oligo/polymerization by using single-site non-metallocene organometallic catalysts with defined substitutions on the heterocycles [7,8].

Another important corollary is mainly from the nature of metal atoms/ions, which collectively offer different properties to catalysts compared with their metallocene counterparts. In this review, we attempt to correlate the recent discoveries and developments in non-metallocene single-site organometallic catalysts bearing aromatic N-heterocyclic scaffolds for use in the production of oligo/polymers from different olefin monomers, ranging from simple α-olefins to conjugated cyclic olefins. Meticulous attention has been paid to the effects of alkyl-metal and aryl-metal catalysts on the rate and yield of oligo/polymerization in comparison with their metallocene counterparts under given reaction conditions. An additional group of important olefin oligo/polymerization organometallic catalysts was developed by the incorporation of a suitable organic or inorganic support such as carbon nanotubes, silica, and alumina [9–11]. Catalysts of this type are more stable than those that are unsupported, and even more insight into this field of research is needed as applications and requirements of these catalysts continue to multiply with particular pressure from commercial interests [12,13].

Over the last decade, increased interest in the development of selective oligomerization and polymerization catalysts has led to a diverse array of catalytic systems based on transition metal complexes, mainly using metallocenes. On the other hand, initial transition metal systems relying on ligands based on mono-Cp motifs linked to arenes and non-metallocene compounds without any metal–carbon linkage have garnered interest in recent studies. However, the importance of systems encompassing a non-metallocene organometallic core with a N-heterocyclic backbone has not been the main focus of any compilation. In this review, the array of successful non-metallocene organometallic transition metal catalysts (groups III–X) based on mononucleating ligands encompassing a N-heterocyclic backbone is discussed with different donor combinations such as NNN, NNO, ONO, PNP, NN, NP, NS, and NO. Synthetic, structural, spectroscopic, X-ray crystallographic, and computational investigations have been performed to gauge the catalytic significance of single-site non-metallocene catalysts bearing N-heterocyclic scaffolds such as pyrazole, pyrrole, imidazole, oxazole, thiazole, benzimidazole, indole, isoindole, pyridine, pyrazine, pyrimidine, and so on, in olefin oligo/polymerization.

2. Scope

The present review focuses on recent developments in the field of olefin polymerization using non-metallocene organometallic catalysts with N-heterocyclic hubs. This is a fairly large section of catalysis that covers the polymerization of simple α-olefins to conjugated cyclic olefins; hence, an attempt is made to consider data even from patents available from online patent databases. The scope is limited to explanations of N-heterocyclic ligands that provide suitable architecture for the ligation to form desired catalysts. In the elucidation section, triazole and tetrazole derivates are excluded as they were not generally used in the formation of active catalysts for the said reactions. Similarly, heterocyclic compounds encompassing more than one type of heteroatom, such as thiadiazole and oxadiazole, are also excluded. Late transition metal catalysts composed of copper or zinc are usually not active for olefin polymerization, and so only those few that are active are included. Ligand and catalyst syntheses, structures, activities towards olefin polymerization, and related mechanisms are discussed, as well as the consequence of these factors on the structures of the resulting polymers. Subjects specifically included are ethylene and norbornene polymerization catalyzed by organometallic catalysts with early transition metals. There have been several recent general ideas in the area of olefin polymerization; hence, there are numerous studies taking place in both academia and industry. A considerable number of additional reviews [14–19] are available in the literature on olefin polymerization with different catalysts and activators [20]. Here, we have attempted to collate the available information on olefin polymerization by non-metallocene organometallic catalysts with N-heterocyclic scaffolds.

Early transition-metal catalysts, such as Ziegler-Natta catalysts, metallocene catalysts, constrained geometry complexes (CGC), and post-metallocene complexes have low compatibility with polar functional groups, such as Brønsted acids and heteroatom-containing functionalities. In particular, polar vinyl monomers are hardly used for early transition-metal catalyzed co-polymerization with non-polar olefins. Since polar vinyl monomers such as acrylates, vinyl ethers, vinyl fluoride, acrylonitrile, and vinyl acetate are commercially important, it is one of the most significant challenges in polymer chemistry to achieve random incorporation of polar vinyl monomers with precise control of polar/non-polar ratios and polymer microstructures [21]. The discrete manipulation of late transition metal catalysts makes it possible to directly co-polymerize polar monomers with non-polar olefins by reducing their oxophilicity and tolerance to other functionalities. Recently, ring-opening metathesis polymer-