Coordination Chemistry Reviews 372 (2018) 101–116

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Developments in compartmentalized bimetallic transition metal ethylene polymerization catalysts

Hongyi Suo [a,b], Gregory A. Solan [a,c,*], Yanping Ma [a], Wen-Hua Sun [a,b,d,*]

[a] *Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[b] *CAS Research/Education Center for Excellence in Molecular Sciences, University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK*
[d] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China*

ARTICLE INFO

Article history:
Received 5 May 2018
Received in revised form 2 June 2018
Accepted 12 June 2018

Keywords:
Bimetallic complex
Early transition metal
Late transition metal
Catalyst
Compartmental ligand
Ethylene polymerization
Polyethylene microstructure

ABSTRACT

Recent progress concerning the application of compartmentalized bimetallic complexes as homogeneous catalysts in ethylene polymerization is reviewed with particular regard to metal-metal combinations based on either early- (Ti, Zr, Hf and V) or late-transition metals (Fe, Co and Ni). The effect of positioning two polymerization-active metal centers in close proximity on catalytic activity, molecular weight, molecular weight distribution and levels of branching are thoroughly documented. Compartmental ligands comprising binding domains consisting of phenoxyimines, *ansa*-bridged cyclopentadienyl-amides, α-diimines and iminopyridines are described as is their capacity to serve as compatible binucleating supports for homobimetallic and also for the less investigated heterobimetallic counterparts. By comparison with their mononuclear analogues, any synergic properties exhibited by these binuclear catalysts represents an underlying theme to be developed where possible throughout this review.

Contents

1. Introduction

The metal-mediated conversion of cheap olefinic monomers (*e.g.*, ethylene, propylene, α-olefins) to highly versatile polyolefinic materials is a field of research with a long and distinguished track

---

* Corresponding authors at: Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

E-mail addresses: whsun@iccas.ac.cn (W.-H. Sun), gas8@leicester.ac.uk (G.A. Solan).

https://doi.org/10.1016/j.ccr.2018.06.006

record. Variations in the particular metal catalyst employed can have dramatic effects on the polymerization process leading to a plethora of important polymers with far reaching uses in the materials industry [1]. Among the types of homogeneous catalyst employed, the bulk of the research effort over the years has been dedicated to the study of systems based on a single metal center drawn from the transition metal series. Indeed, this type of catalyst has been the subject of many excellent reviews, some of the more recent examples being referenced herein [2–5]. With regard to late transition metal catalysts for ethylene polymerization, numerous studies have been directed towards modifying the classic bis(imino)pyridine supporting ligand by changing the substituents of the imino-linked N-aryl moieties [6,7] as well as the substituents on the imine-carbon atom [8–12]. One major breakthrough was establishing that sterically bulky groups tend to promote polymer chain growth over chain transfer by blocking coordination sites on the metal complexes [13,14].

As an emerging strategy within the polymerization arena, the bimetallic approach in which two polymerization-active metal centers are compartmentalized on the same ligand framework, has been attracting growing attention. This can, in part, be attributed to the promising cooperative effects [15,16] imparted by the close proximity of the two metal centers which is not achievable with a mononuclear catalyst. Indeed, bimetallic olefin polymerization catalysts can exhibit remarkable synergic effects in catalytic activity, polymer microstructure (*e.g.*, molecular weight, chain branching, monomer repeat regioregularity) as well as selectivity for co-monomer enchainment [1]. Several examples have now been disclosed suggesting the importance of cooperativity between metallic sites in the development of new catalysts [17–19].

In the late 1990s, it was shown that certain phenoxyimine compounds (**I** in Chart 1) could serve as compatible ligands for both early and late transition metal olefin polymerization catalysts. In particular, the so-called FI-group IV catalysts, when suitably activated, exhibit unprecedented catalytic activities for the polymerization of ethylene [20,21]. Meanwhile, phenoxyimine-nickel complexes have displayed not only high catalytic activity but also good functional group tolerance [16]. By providing a suitable steric environment around the nickel center through the introduction of strategically placed substituents on **I**, chain transfer reactions via β-H elimination can be suppressed leading to the production of high molecular weight polymers [13].

Elsewhere, complexes containing a cyclopentadienyl-silyl-amido ligand scaffold (**II** in Chart 1), later named constrained geometry catalysts (CGCs), have proved industrially relevant catalysts based on early transition metals [22]. Importantly, polymerizations with these species can be carried out at high reactor temperatures when activated with the appropriate co-catalyst [23]. They can be described as efficient ethylene polymerization catalysts with high polymerization activities and the unusual capacity to enchain bulky co-monomers, which reflects the sterically open, coordinatively unsaturated architectures. Moreover, high molecular weight polymers can be obtained due to the relatively slow rates of chain transfer [1].

Late transition metal catalysts bearing numerous types of neutral imine-based N,N,N and N,N ligands have been well documented since their emergence in the mid to late 1990s. Indeed, the prototypical bis(arylimino)pyridine (**III**, Chart 1) and α-diimine (**IV**, Chart 1) remain the benchmarks and continue to be the source of new developments. Indeed, examples of iron and cobalt catalysts bearing **III** have now emerged that not only exhibit exceptional performance and high thermal stabilities but are also capable of promoting a broad range of oligomer and polymer properties [12,24,25]. Furthermore, these types of catalyst can produce polymers incorporating a range of branching contents [11,26].

In this review, we are concerned with binuclear early and late transition metal complexes that incorporate binding domains based on mainly the chelation pockets found in **I**–**IV** (Chart 1). Considerable effort will be made to correlate effects of catalyst structure on polymerization activity, molecular weight, molecular weight distribution and branching content. In addition, any cooperative effects imparted by the presence of the two closely located metal centers will be fully discussed.

2. Binuclear early transition metal catalysts for ethylene homo- and copolymerization

Homobimetallic group 4 catalysts based on phenoxyimine [27,28] and cyclopentadienyl-silyl-amido ligands (Ti_2 [29–31], Zr_2 [19,32,33]), have been shown to exhibit distinctive cooperative effects by producing polyolefins with substantially higher molecular weights when compared to their corresponding monometallic analogues. In addition, heterobimetallic systems (TiZr, [34] TiCr [35,36]) based on cyclopentadienyl-silyl-amido ligands have also been reported (*vide infra*).

Phenoxyimine catalysts demonstrate excellent performance in terms of both catalytic activity and stereocontrol in olefin polymerization [37]. Ma's group has synthesized the binuclear hetero-ligated titanium catalysts (**1** and **2**, Fig. 1) for ethylene polymerization and copolymerization [37]. The molecular structure of **1** shows that this bimetallic molecule possesses a tweezer-like structure exhibiting C_2 symmetry with the distance between the two titanium atoms being 7.88 Å, which suggests significant repulsive interactions between the two catalytic sites. The catalytic activity of **1** can reach up to 2.95×10^6 g mol^{-1} h^{-1} with the polymer displaying a narrow PDI of 1.71 and a M_w of up to 1.7×10^2 kg mol^{-1}. In comparison, its mononuclear counterpart exhibited slightly higher activity (3.12×10^6 g mol^{-1} h^{-1}) with a narrower PDI (1.66) along with higher M_w (1.9×10^2 kg mol^{-1}). On the other hand, **2** though displaying quite low activity, showed superior results in terms of activity, PDI and molecular weight when compared with its mononuclear counterpart (activity: 1.6×10^4 g mol^{-1} h^{-1} *vs.* 0.6×10^4 g mol^{-1} h^{-1}, PDI: 3.26 *vs.* 49.3 and M_w: 6.4×10^2 kg mol^{-1} *vs.* 5.1×10^2 kg mol^{-1}). In addition, both **1** and **2** can copolymerize ethylene with monoenes and dienes.

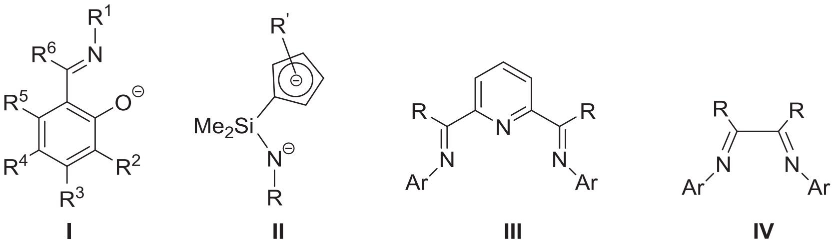

Chart 1. The four main types of chelating ligand highlighted in this review.