Development of Strikingly Active Catalysts for the Selective Trimerization of Ethylene to 1-Hexene Based On FI Catalysts for Olefin Polymerization

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Abstract: A family of phenoxy-imine-ether ligated Ti catalysts for selective ethylene trimeriation have been developed based on highly active bis(phenoxy-imine) early transition metal olefin polymerization catalysts (a.k.a. FI catalysts). The best catalyst produces 1-hexene with 93.3 wt% selectivity and exhibits an exceptionally high productivity of 31.9 kg of 1-hexene/mmol-Ti·h under an ethylene pressure of 0.8 MPa, representing one of the highest performing ethylene trimerization catalysts reported to date. This selective ethylene trimerization catalyst technology has already been commercialized at Mitsui Chemicals.

Keywords: Ethylene trimerization, 1-hexene, FI catalysts.

1. Introduction

1-Hexene is an industrially significant α-olefin in that it is a pivotal comonomer for the production of ethylene-based polymers, represented by linear low-density polyethylene. However, it is generally obtained in only 10 to 20 wt% selectivity by the catalytic oligomerization of ethylene because this oligomerization affords α-olefins of various chain lengths usually following a Schulz-Flory distribution which does not match market demand for each α-olefin.

Evidently, the most straightforward method to prepare 1-hexene is the selective trimerization of ethylene. Since the first report on Cr-catalyzed selective ethylene trimerization1), intensive research has focused on the development of new ethylene trimerization catalysts, resulting in the introduction of high performance catalysts based on Cr, Zr, Ti, and Ta metals2). In 2003, a Cr-and-pyrrole-based catalyst was commercialized in Qatar by Chevron-Phillips. Recently, attention has been directed towards the development of even newer catalysts that provide higher catalyst productivity.

2. Catalyst design for selective ethylene trimerization

While the mechanisms for ethylene oligomerization/polymerization (Cossee-Arlman mechanism) and selective ethylene trimerization (metallacyclic mechanism) are seemingly different to one another, both are based on a process that involves intense electron exchange between a ligand and a metal in order to stabilize the catalyst species. We, therefore, postulated that highly active ethylene polymerization catalysts possess significant potential for selective ethylene trimerization3,4). Thus, we aimed at developing selective ethylene trimerization catalysts based on bis(phenoxy-imine) early transition metal olefin polymerization catalysts (a.k.a. FI catalysts5-7)) that display the highest catalytic productivity of any artificial catalyst for ethylene polymerization to date. By the appropriate modification of the FI catalyst in terms of redox property (metal selection and ligand structure) and reaction site number (ligand structure), we designed Ti complexes having a single FI ligand with a pendant neutral donor (L) (Fig. 1), as viable selective ethylene trimerization catalysts.

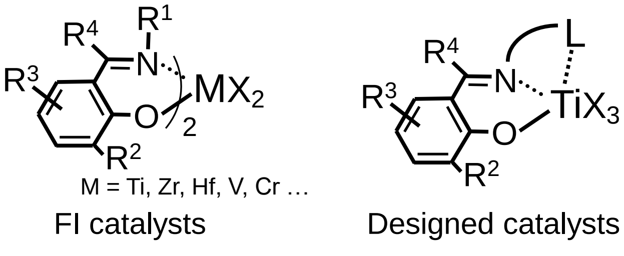

Figure 1. FI catalysts and designed catalysts for selective ethylene trimerization based on FI catalysts

3. Results and discussion

Catalyst design based on FI catalysts worked well, so that during the course of the synthesis and evaluation of the Ti complexes having a single FI ligand with a pendant neutral donor, we came upon Ti complex A (Fig. 2) bearing a phenoxy-imine-ether ligand. This complex, when activated with methylaluminoxane (MAO), formed 1-hexene (34.5 wt% selectivity, and ca. 100 wt% selectivity among the ethylene oligomers produced) in addition to polyethylene (65.5 wt% selectivity) though it displayed a moderate activity of 0.1 kg of product/mmol-Ti·h (ethylene pressure 0.8 MPa)8).

Subsequent research focusing on Ti complexes having a phenoxy-imine-ether ligand resulted in the discovery of Ti complexes B possessing an aryl-based ether donor. These complexes with MAO exhibited remarkable catalytic properties, and selectively furnished 1-hexene with high efficiency8-10). We have given the name SFI catalysts to these high performance catalysts for the formation of 1-hexene. The best SFI catalyst produces 1-hexene with a selectivity of 93.3 wt% and a productivity of 31.9 kg of 1-hexene/mmol-Ti·h under an ethylene pressure of 0.8 MPa7). This productivity is two orders of magnitude higher than that for common chromium-based catalysts under similar conditions, and simultaneously, one of the highest values reported to date.

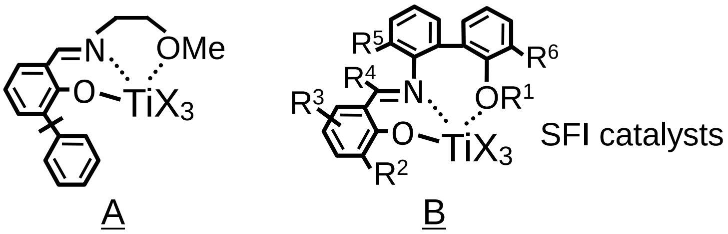

Figure 2. Ti complex A and Ti complexes B (SFI catalysts).

In addition, DFT calculations have given mechanistic insights into the formation of a catalytically active Ti(II) species as well as that of 1-hexene. Additionally, the calculations provided useful information on the preference for the selective ethylene trimerization; namely, selective 1-hexene formation, with SFI catalysts8). These calculation results gave tips on the development of higher performance SFI catalysts and on the development of selective ethylene dimerization and tetramerization catalysts.

4. Conclusions

This selective 1-hexene production technology utilizing SFI catalysts has already been commercialized at Mitsui Chemicals' Ichihara Works, Chiba, Japan, thus representing the first example of 1-hexene manufacture using a non-Cr-based catalyst. The impact of the development of SFI catalysts is that they have introduced a new family of high performance selective ethylene trimerization catalysts to the petrochemical market place, and inspired a large number of researchers to make significant contributions towards the further development of the steadfast SFI catalysts.

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