

Development of High Activity Catalysts for Selective Ethylene Trimerization to 1-Hexene.

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Ethylene oligomerization normally results in the formation of a range of α -olefins following a Schulz-Flory distribution. Therefore, the development of catalysts capable of selectively oligomerizing ethylene to a desired α -olefin would be of great value. In particular, the selective trimerization of ethylene to 1-hexene has received a lot of attention because of the great importance of this α -olefin in the manufacture of ethylene-based copolymers such as high-density polyethylene (PE), linear low-density PE, and plastomers.

As a result, a lot of high performance catalysts have been developed based on transition metals, such as chromium, titanium, zirconium, and tantalum [1], and since 2003, the chromium-based Phillips catalyst has been commercialized.

Regarding olefin polymerization catalysts, Mitsui Chemicals has developed a number of highly active ethylene polymerization catalysts (Fig. 1), most notably, the phenoxy-imine-ligated early transition metal catalysts (FI catalysts), and the pyrrolide-imine-ligated group 4 transition metal catalysts (PI catalysts) [2], both of which are based on the concept where the electronically flexible properties of the ligands play a crucial role in achieving high activity, given the fact that the polymerization process involves an intense electron exchange between a ligand and a metal, as is indicated by DFT calculations.

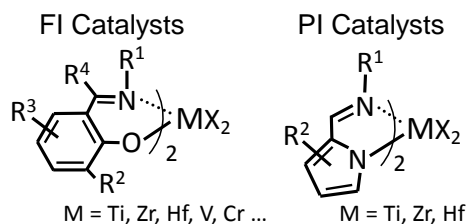


Fig.1 FI Catalysts and PI Catalysts

Although the mechanisms for ethylene polymerization (the Cossee-Arlman mechanism) and selective ethylene trimerization (the metallacyclic mechanism) are different, both are based on a process involving an intense electron exchange. Thus, we at Mitsui Chemicals believe that a ligand that produces a high activity catalyst for ethylene polymerization should still form a

high activity catalyst for selective ethylene trimerization after the appropriate modification of the ligand in terms of its coordination number and electron donating ability.

Thus it is, at Mitsui Chemicals, we have developed a number of highly active ethylene trimerization catalysts, on the basis of our ligand-oriented catalyst design concept, indicative of the importance of the electronically flexible properties of ligands, in order to update ethylene trimerization efficiency. Of these, titanium catalysts possessing a phenoxy-imine ligand with a pendant ether donor (Fig. 2) affords 1-hexene with very high selectivity and productivity [3]. We have appropriately named these catalysts "SFI catalysts" because Selective ethylene trimerization catalysts are FI ligand-based.

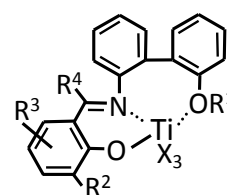


Fig. 2 Structure of SFI Catalysts

The best SFI catalyst produces 1-hexene with a selectivity of 92% and an activity of 6,590 kg/g-Ti/h at 50 bar ethylene pressure, which is two orders of magnitude higher than for common chromium-based catalysts under similar conditions, and simultaneously, one of the highest values reported to date. This SFI catalyst technology has already been commercialized. Recent studies conducted by Bercaw, Duchateau, and others have made significant contributions to the further development of SFI catalysts [4].

In this lecture, we would like to describe the development of high activity selective ethylene trimerization catalysts to 1-hexene, and at the same time, introduce the mechanism behind 1-hexene formation with SFI catalysts.

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