IPPI
Polyolefins Journal, Vol. 2 No. 1 (2015) 17-25
REVIEW PAPER

Intelligent catalysts for ethylene oligomerization and polymerization

Helmut G. Alt*

Laboratorium für Anorganische Chemie
Universität Bayreuth, 95440 Bayreuth, Germany

Received: 27 October 2014, Accepted: 1 December 2014

ABSTRACT

Ethylene polymerization catalysts became available in an enormous variety. The challenge in this research is to find catalysts that are able to connect ethylene molecules in such a way that not only linear chains are produced but variations like branched materials that possess very interesting mechanical properties like linear low density polyethylene (LLDPE). In this contribution, three different types of catalysts are presented that are able to do not only one job at a time but three. These are “intelligent catalysts”. Catalysts of type 1 are homogeneous metallocene complexes that can be activated with methylaluminoxane (MAO). With ethylene they produce their own support and they become heterogeneous catalysts (self-immobilization) and they prevent fouling in polymerization reactors. The produced resin has evenly distributed ethyl branches (without a comonomer) with unique properties and the MAO that is necessary in the activation step can be recycled. Catalysts of type 2 are dinuclear complexes with two different active sites. One centre can oligomerize ethylene and the other one can copolymerize the in statu nascendi produced oligomers with ethylene to give branched LLDPE (a molecule as the smallest reactor for LLDPE) and/or bimodal resins. Catalysts of type 3 are MAO activated iron di (imino) pyridine complexes that are able to oligomerize ethylene to give not only oligomers with even numbered carbon atoms but also odd numbered ones. In this reaction, one catalyst does three jobs at a time: oligomerization, isomerization and metathesis of ethylene. **Polyolefins J (2015) 2: 17-25**

Keywords: multi talented catalysts; oligomerization; polymerization; metathesis of ethylene; metallocene catalysts; di(imino) pyridine catalysis

---

INTRODUCTION

One trend in modern catalyst research is the design of catalysts that are able to produce tailored products in an efficient manner. In olefin polymerization, ethylene is the mostly used monomer and worldwide nearly 100 million tons of various types of polyethylenes are produced [1-4]. The challenge in this research is to find catalysts that are able to connect ethylene molecules in such a way that not only linear chains are produced but variations like different branchings or resins with bi- or multimodal molecular weight distributions. In the past 25 years my research group prepared and characterized more than 1600 different catalysts for olefin oligomerization, olefin polymerization and CH activation reactions. In this review from this research team three different types of catalysts are presented that can do more than one job at a time. I call them intelligent catalysts.

RESULTS AND DICUSSION

Catalysts for olefin oligomerization and polymerization should fulfill the following challenges:

---

* Corresponding Author - E-mail: helmut.alt@uni-bayreuth.de

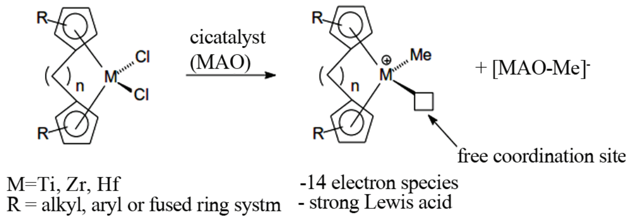


Figure 1. Activation reaction of a metallocene dichloride complex with methylaluminoxane (MAO)

They should
- have high activities,
- be able to become heterogenized,
- have the potential to oligomerize ethylene to give 1-butene, 1-hexene, 1-octene α-olefins for copolymerization reactions,
- be able to do more than one job at a time (i. e. intelligent catalysts),
- be able to produce new resins with superior properties to create new markets.

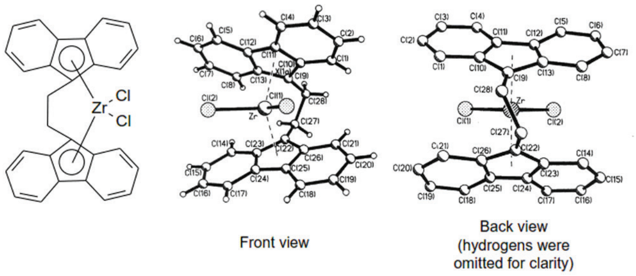


Figure 2. A 1,2- ethylidene bridged bis(fluorenyl) complex of zirconium

Metallocene complexes became very attractive over the past 25 years. They can be activated with methylaluminoxane (MAO) [5, 6] and the resulting cationic species is discussed as the actual catalyst for olefin polymerization.

We showed that bridged bis(fluorenyl)zirconium complexes are excellent catalysts for ethylene polymerization and they are record-holders in activity [7]. The main reason seems to be the “ring slippage” behaviour [8] of these ligands providing very low activation energies for the various steps in polymerization reactions.

The catalyst properties, like molecular weights of the produced polymers and the activities, can be tuned

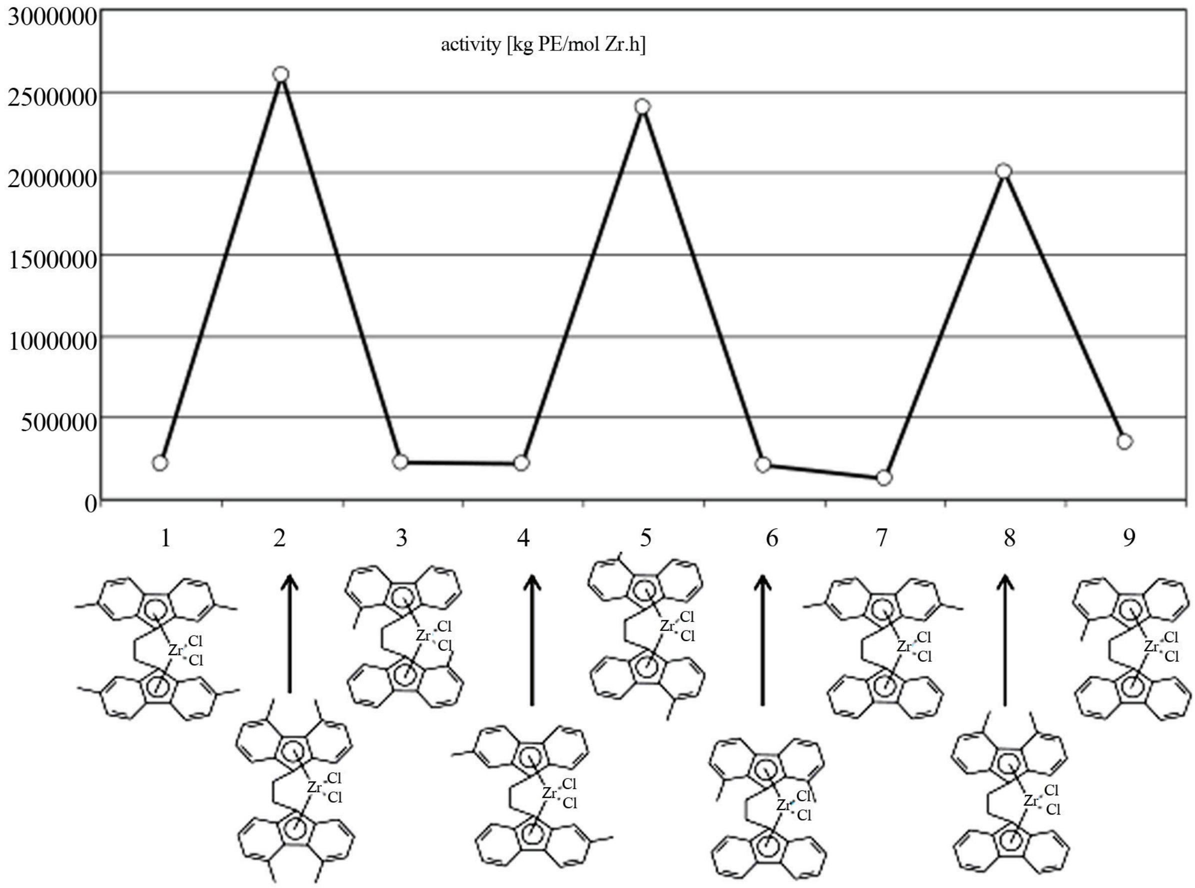
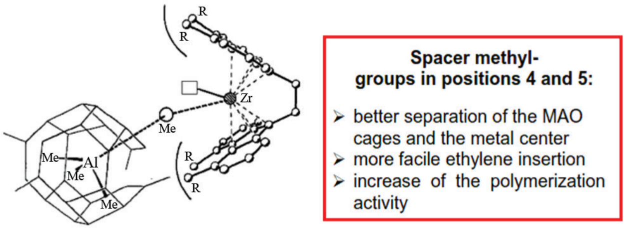


Figure 3. Influence of the positions of methyl substituents in 1,2- ethylidine bridged bis(fluorenyl) complexes on the polymerization activities



Spacer methyl-groups in positions 4 and 5:

- better separation of the MAO cages and the metal center
- more facile ethylene insertion
- increase of the polymerization activity

Substituent	Activity [kg PE/mol Zr.h]	Molecular weight (PE) [g/mol]
R – H	420 000	620 000
R – Me	2 700 000	440 000

Figure 4. The spacer effect of methyl substituents in activated *ansa*-bis (fluorenyl) complexes

via structure property relationships, i.e. tiny changes in the catalyst molecule can have drastic consequences in the performance of such homogeneous catalysts. The following example demonstrates how the positions of methyl substituents on a fluorenyl ligand can determine the activity of a catalyst [3].

Methyl substituents in the 4- and 5- positions of this ligand act like spacers and keep the spacious MAO anion away from the active centre. In this way there is sufficient room for the coordinating monomer and even more important, enough room for the growing polymer chain.

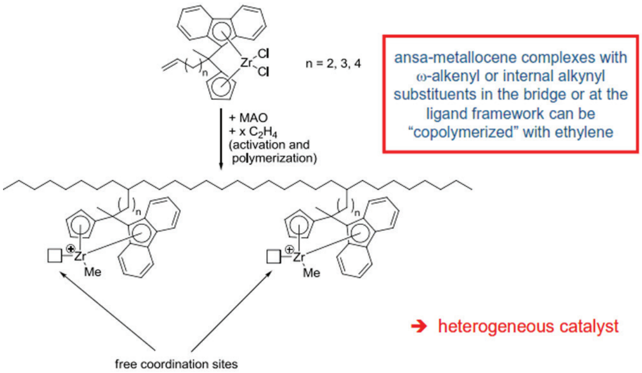


Figure 6. Self-immobilization of a metallocene catalyst

Indeed, from about 800 metallocene catalysts prepared in my research group, the top seven in terms of activity are fluorenyl complexes [3].

These bridged bis(fluorenyl)zirconium complexes are excellent ethylene polymerization catalysts but they can perform only one reaction: ethylene polymerization.

When we were looking for a way to heterogenize homogeneous ethylene polymerization catalysts in order to avoid “reactor fouling” and in order to avoid already existing patents for various support materials, we invented self-immobilizing catalysts [9-12]: these are not only catalysts but also olefins because they

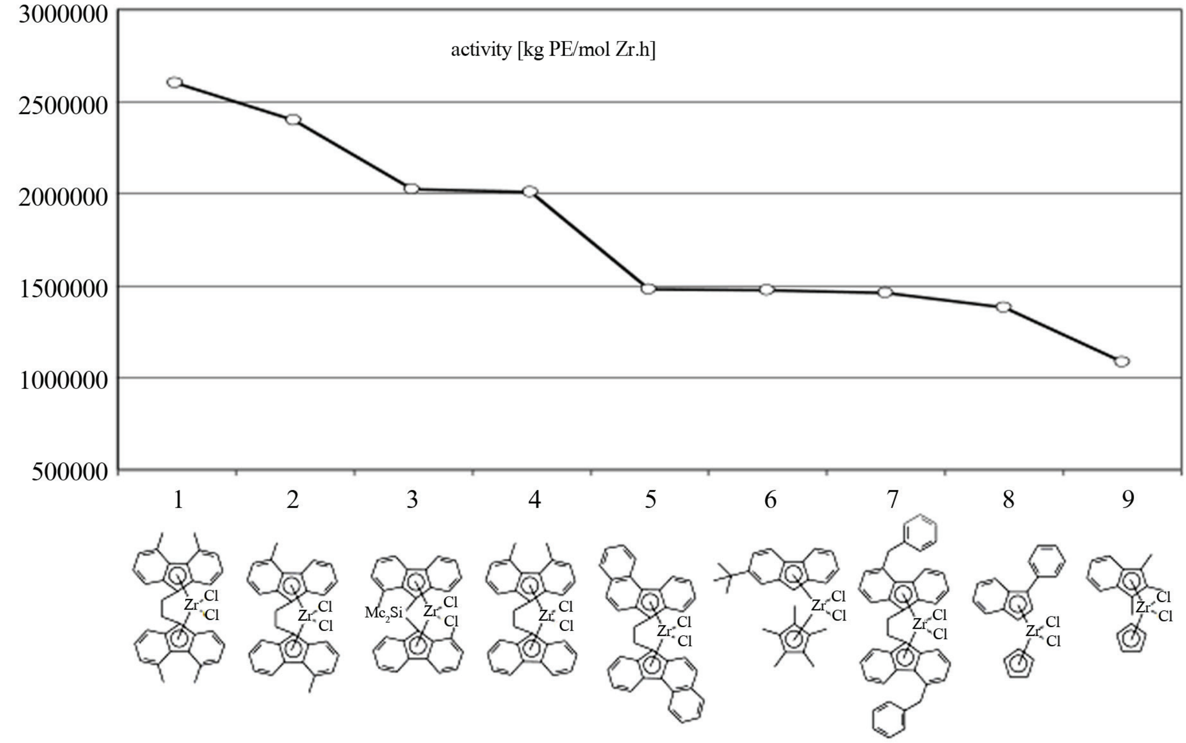


Figure 5. Top 9 of the most active metallocene complexes for catalytic ethylene polymerization

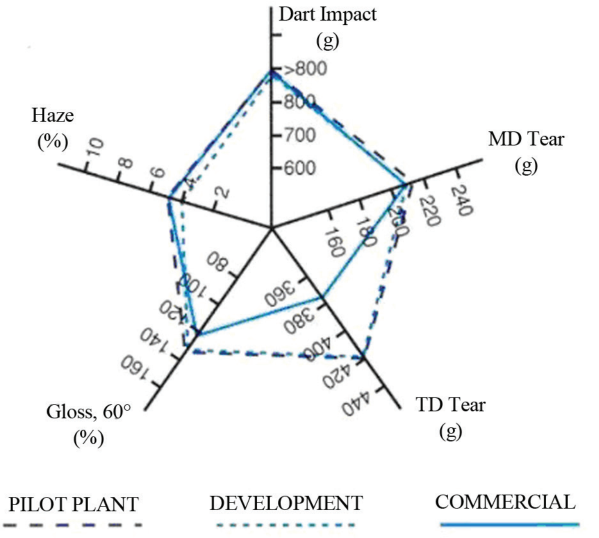


Figure 7. Film properties of m-LLDPE resins (0.918 g/cm³, ~1 M¹)

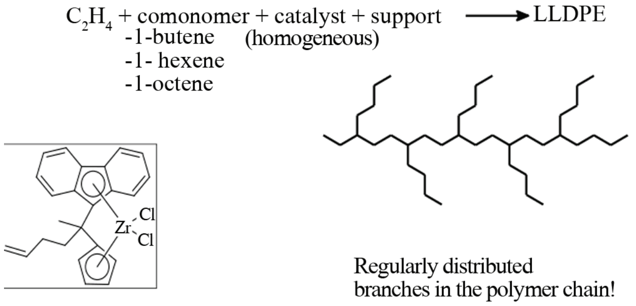


Figure 9. A conventional way to produce linear low density polyethylene (LLDPE)

have an olefin function in the ligand framework.

Upon activation of such catalyst precursors with MAO in a homogeneous solution, the catalyst molecule starts to polymerize ethylene as soon as this monomer is added to the solution. But it obviously also copolymerizes the catalyst molecules because of their olefin function. As a consequence, a multinuclear three-dimensional heterogeneous catalyst network is formed that can be considered as a prepolymerized catalyst and that is completely heterogeneous. It can be filtered, washed with toluene, dried and stored for years in steel drums without losing its activity. It is a drop-in catalyst. In other words, this catalyst produces its own support, it is self-immobilizing and it does not need other support materials that could reduce the activities of such catalysts because of their Lewis basic surfaces.

As an additional benefit, the applied MAO can be recycled because it consists of a dynamic equilibrium of various components and the active species, which seems to be an MAO cage with monomeric trimethylaluminum in the inside is generated for other activation runs. When the polymer was characterized it turned out that the formed resin (m-Pact, from ChevronPhillips, USA) was not a simple linear polyethylene but an ethylene with evenly distributed ethyl branches, and this without the application of any comonomers. Obviously, the polymerization mechanism proceeds in a way that metallacycles are formed and undergo ß-hydrogen elimination reactions once they have reached a certain size and thus form evenly distributed ethyl branches. In addition, such catalysts allow copolymerization with other olefins like 1-butene or 1-hexene to give different brands of LLDPE.

The produced resin has superior properties to other

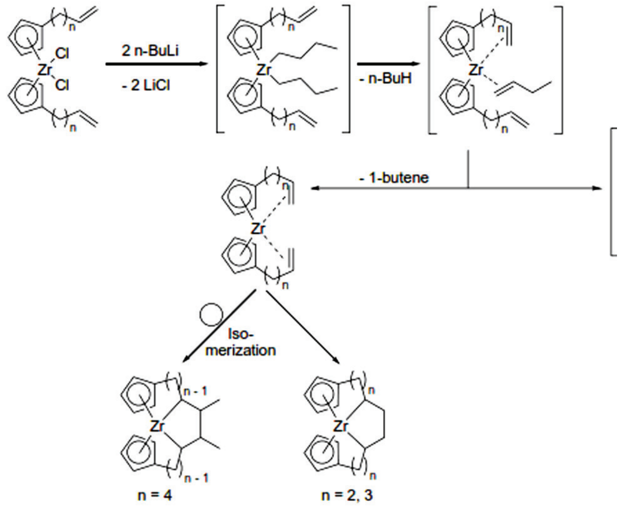


Figure 8. Metallacycles from alkenyl substituted metallocene complexes (halogen free catalysts)

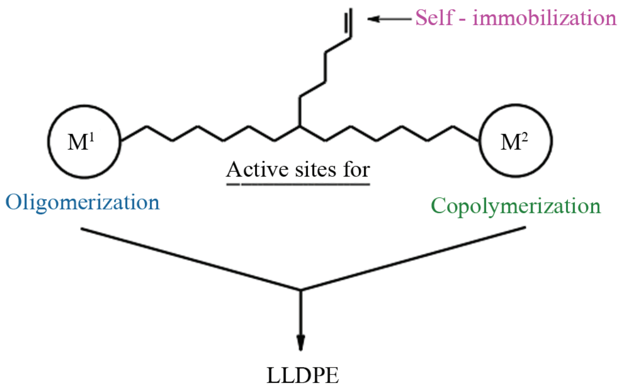


Figure 10. Dissymmetric dinuclear complexes with the potential of intelligent catalysts

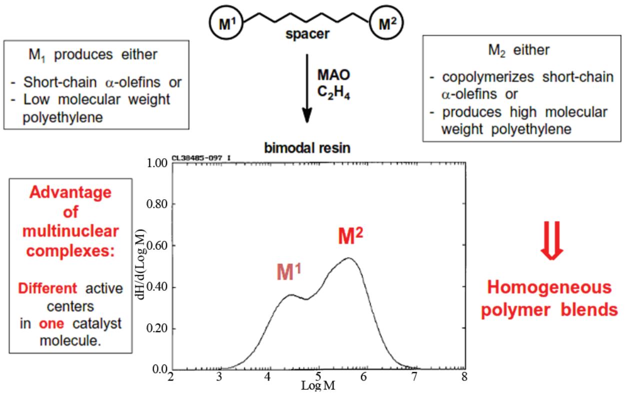


Figure 11. Dinuclear complexes as catalysts for the production of bimodal resins

LLDPE brands in the market as depicted in Figure 7.

Indeed, this is an intelligent catalyst because one and the same catalyst can polymerize ethylene. In addition, it produces its own support and it generates evenly distributed ethyl branches at the polymer main chain without any comonomer.

Catalysts with very similar properties are metallacycles that can be prepared according to Figure 8 [13, 14].

Upon activation with MAO the metallacycle opens up and a cationic catalyst containing an olefin function is formed. In this way, such catalysts can also be copolymerized and form a three dimensional network as described before. The advantage of the formed polyethylenes is the fact that they do not contain any halides (from the catalyst precursors) and therefore they do not produce any corrosive products if they are thermally recycled.

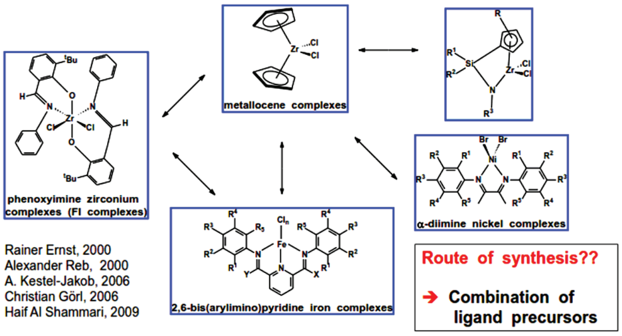


Figure 12. Combination possibilities of mononuclear catalyst precursors

Such catalysts offer a convenient approach to LLDPE. In order to make such a way even more general, a solution was found using binuclear or multinuclear catalysts. The conventional way to make LLDPE needs the monomer, a comonomer, a catalyst and a support material in order to avoid fouling in the reactor.

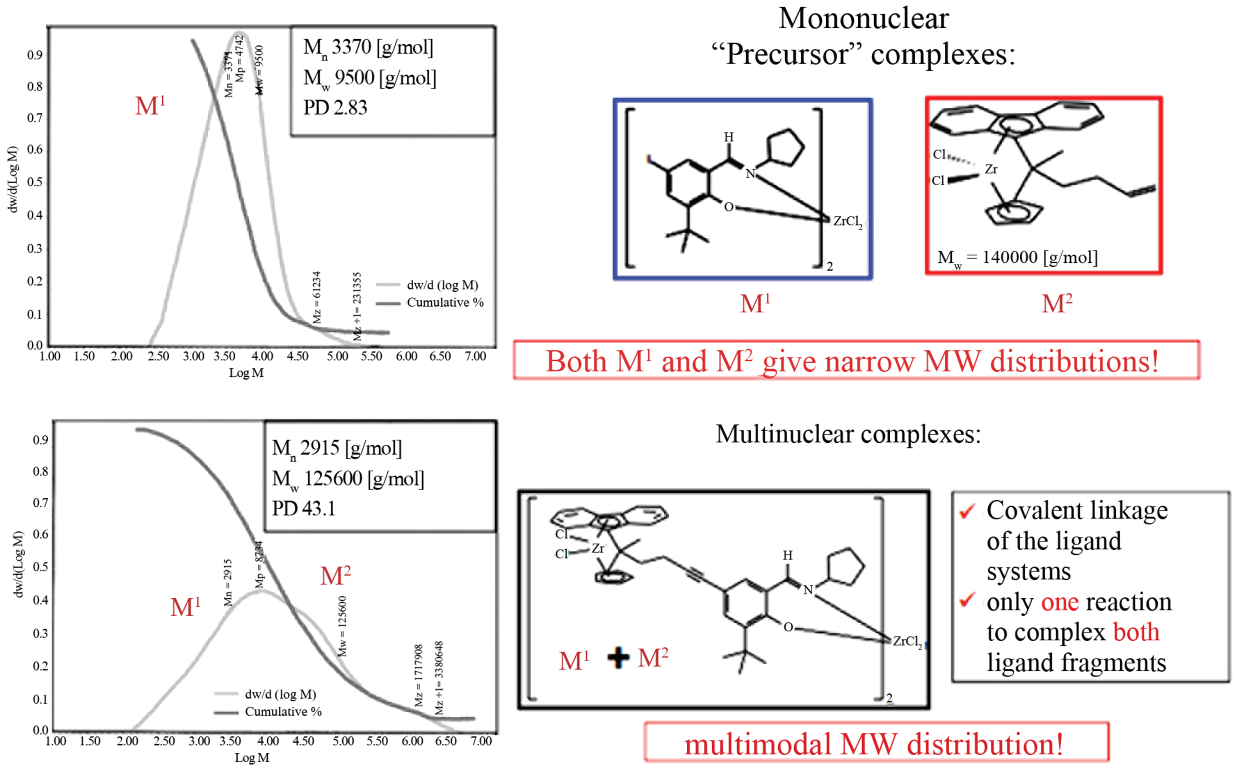
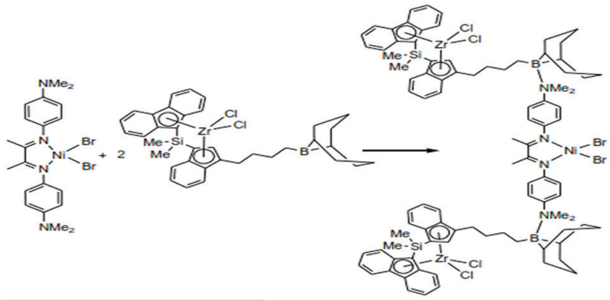


Figure 13. An example for the "tuning" of polyethylene properties



Donor-acceptor catalyst system:
- metallocene complex containing electron acceptor atom
- Ni diimine complexes bearing electron donor atom.

After activation with MAO, the metallocene part produces PE with high molecular weight while the Ni diimine part produces PE with low molecular weight.

Figure 14. Combination of donor/acceptor catalysts for the production of polyethylenes with bimodal molecular weight distributions

The strategy was to start with a dinuclear complex that consists of two different active sites and an olefin function in the catalyst molecule.

The active site M^1 in the catalyst molecule is able to oligomerize ethylene and to produce oligomers. The active site M^2 is able to polymerize ethylene but also to copolymerize the in-situ-produced oligomers of M^1. For this purpose, the distance between M^1 and M^2 is crucial. The olefin function in the molecule provides the self-immobilisation capability of the system. This molecular set-up reminds one to modern automobile assembly methods: delivery of the necessary parts just in time. Such intelligent catalyst molecules that can produce their own comonomers, their own support and LLDPE with special properties can be considered as the smallest plants for LLDPE because these plants are molecules. This is also an ultimate nanotechnology.

Since my research group has a pool of more than 1600 catalyst precursors, there are numerous possibilities to connect various mononuclear catalyst precursors to reach certain goals.

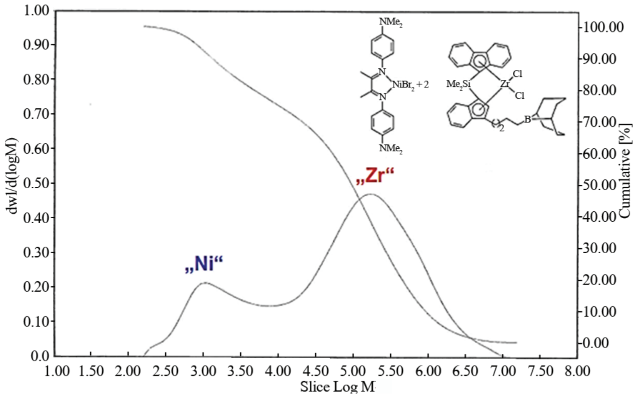
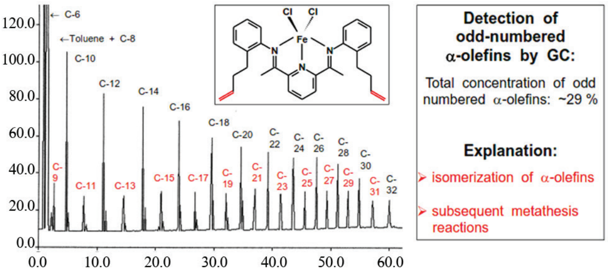


Figure 15. Trinuclear donor/acceptor catalyst for the production of bimodal polyethylene



Detection of odd-numbered α-olefins by GC:

Total concentration of odd numbered α-olefins: ~29 %

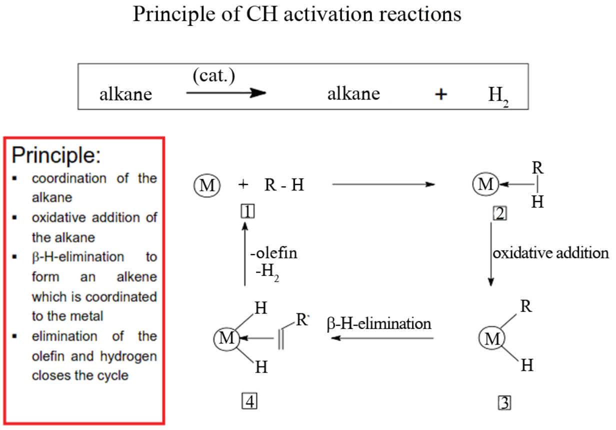
Explanation:
- isomerization of α-olefins
- subsequent metathesis reactions

Figure 16. Catalytic production of olefins with odd numbers of carbon atoms from ethylene

One approach is to make resins with bimodal molecular weight distributions. Since many homogeneous catalysts produce polymers with a narrow molecular weight distribution, bimodal resins are necessary for good polymer processibility. With this method perfect homogeneous blends can be prepared on a molecular scale.

Examples for the combination possibilities are given in Figure 12. One has the choice between the following coupling candidates: metallocene complexes, half-sandwich complexes, phenoxyimine complexes, bis(arylimino)pyridine complexes and diimine nickel complexes [15-17].

A good example for the tuning of polyethylene properties is the application of a dinuclear catalyst precursor consisting of a metallocene unit and a phenoxyimine unit [13]. M^1 of the mononuclear phenoxyimine component produces polyethylene with a comparatively low molecular weight of M_w = 9500 g/mol and a narrow molecular weight distribution of 2.83. M^2 of the mononuclear metallocene unit generates a much higher molecular weight of M_w = 140000 g/mol and a similar narrow molecular weight


Principle of CH activation reactions

alkane $\xrightarrow{\text{(cat.)}}$ alkane + H_2

Principle:
- coordination of the alkane
- oxidative addition of the alkane
- β-H-elimination to form an alkene which is coordinated to the metal
- elimination of the olefin and hydrogen closes the cycle

Figure 17. Principle of catalytic CH activation

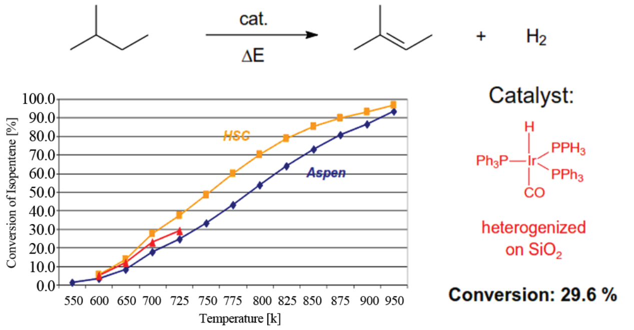


Figure 18. Catalytic dehydrogenation of isopentane without a hydrogen acceptor

distribution. The dinuclear catalyst consisting of these two components produces polyethylene with a M_w = 125600 and a broad PD = 43.1. The dinuclear catalyst precursor can be synthesized as indicated in Figure 13.

Another convenient approach is the combination of catalyst precursors with substituents that have a Lewis acid character and those with a Lewis base character as indicated in Figure 14 [18].

Mononuclear metallocene complexes with donor/acceptor properties are known in the literature and they are famous because of their dynamic properties in ethylene polymerization [19, 20].

Figure 15 presents the properties of the resulting polyethylene: a bimodal resin that its lower molecular weights are produced from the nickel containing catalyst and its higher molecular weights from the zirconium containing unit.

In this context, the question arises that it would be easier to mix the corresponding mononuclear catalyst precursors in order to obtain the same results. In addition, the ratio of the mixed components could be another helpful parameter for the design of polyolefin properties. Unfortunately, this method does not work in most cases [21]. Obviously, the various active species interact in a way that a polyolefin with averaged properties is resulted but not with the desired ones.

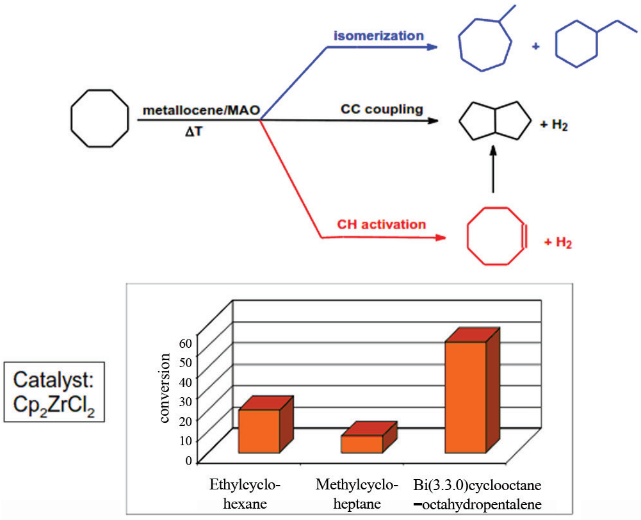


Figure 19. Activation of cyclooctane with a "metallocene catalyst"

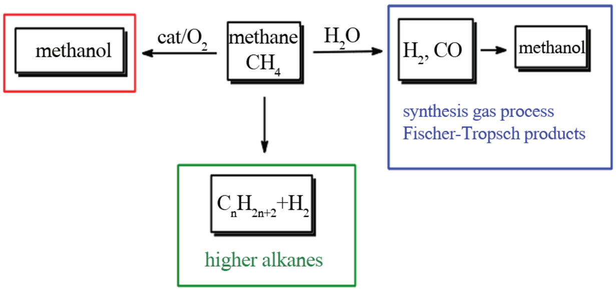


Figure 20. Methane (= natural gas) as an inexhaustible feedstock for the catalytic production of higher hydrocarbons and methanol

In order to provide a good selection of catalysts that are able to oligomerize ethylene selectively, we prepared various iron di(imino)pyridine complexes [17]. The big surprise was that some of them not only oligomerize ethylene to give even numbered oligomers like 1-butene, 1-hexene, 1-octene, etc but also oligomerize it to give oligomers with odd numbers of carbon atoms such as 1-heptene, 1-nonene, 1-undecene, etc. (see Figure 16).

How is this possible? Our explanation is that one and the same active site can do three jobs at a time: to oligomerize ethylene and generate higher 1-olefins with even numbers of carbon atoms. The same active site is able to isomerize these oligomers to form 2-olefins and these 2-olefins undergo metathesis reactions with etylene at the same active site to produce the oligomers with the odd numbers of carbon atoms. This result was an "accident" because it was not expected and at the same time a good reason to remember the old wisdom to keep the eyes open when research results are analyzed.

The presented examples are all discussed in the literature but it is worth to consider intelligent catalysts for future demands. I consider one of the highest challenges in the field of catalysis the selective activation of alkanes and to make olefins and hydrogen. Olefins are the main feedstock of industrial organic chemistry and alkanes are the cheapest starting materials. The mechanism could proceed according to Figure 17.

Recently we could realize such a reaction with isopentane, a low boiling hydrocarbon (b.p. 28°C) that is no longer allowed as gasoline component. With the right catalyst it can be dehydrogenated [22] and the resulting isopentene can be dimerized catalytically to give a valuable gasoline component with a high octane number.

A big surprise was the fact that metallocene catalysts are also able to activate alkanes in isomerization reactions, CC coupling reactions and CH activation reactions as presented in Figure 19 [23, 24].

However, the metallocene catalyst is not a usual metallocene catalyst: it is a “decomposed metallocene catalyst” that was obtained by heating it to 300°C. At this temperature, a new species has been formed that was responsible for the activation of hydrocarbons like cyclooctane and others.

The ultimate goal would be to invent the catalytic activation of methane to obtain higher hydrocarbons and hydrogen or the selective oxidation of methane to give methanol without using a Fischer-Tropsch process.

In both cases liquids would be the products from natural gas, which represents the richest resource of energy on this planet.

CONCLUSIONS

It is a very attractive approach to design catalysts in a way that they can perform all the tasks that are necessary to obtain products with the desired properties. In this review various paths have been described how to achieve such challenges. Intelligent catalysts can do more than one job at a time when one active site is flexible enough to perform different reactions such as oligomerization, isomerization, polymerization and metathesis. Another solution is to combine different mononuclear complexes in a way that dissymmetric binuclear or multinuclear complexes with different active sites are formed. Every active site can then produce its own typical product on a molecular scale (molecular reactor, nano technology).

REFERENCES

1. Severn JR, Chadwick JC, Duchateau R, Friederichs N (2005) bound but not gagged immobilizing single-site α-olefin polymerization catalysts. Chem Rev 105: 4073-147
2. Kaminsky W (2008) Google archiv. Aktuelle wochenschau.de 48. woche
3. Alt HG, Köppl A (2000) Effect of the nature of metallocene complexes of group IV metals on their performance in catalytic ethylene and propylene polymerization. Chem Rev 100:1205-1222
4. Severn JR, Chadwick JC (2008) Tailor-Made Polymers, Wiley-VCH
5. Sinn H, Kaminsky W, Vollmer HJ (1980) Lebende Polymere bei Ziegler Katalysatoren extremer Produktivität. Angew Chem 92: 396-402
6. Sinn H, Kaminsky W (1980) Ziegler-Natta catalysis. Adv Organomet Chem 18: 99-149
7. Alt HG, Milius W, Palackal SJ (1994) Verbrückte Bis(fluorenyl)komplexe des Zirconiums und Hafniums als hochreaktive Katalysatoren bei der homogenen Olefinpolymerisation. Die Molekülstrukturen von $(C_{13}H_9\text{-}C_2H_4\text{-}C_{13}H_9)$ und $(\eta_5{:}\eta_5\text{-}C_{13}H_8\text{-}C_2H_4\text{-}C_{13}H_8)ZrCl_2$. J Organomet Chem 472:113-118
8. Alt HG, Samuel E (1998) Fluorenyl complexes of zirconium and hafnium as catalysts for olefin polymerization. Chem Soc Rev 27: 323-329
9. Peifer B, Milius W, Alt HG (1998) Verbrückte indenyliden–cyclopentadienylidenkomplexe des typs $(C_9H_5CH_2Ph\text{–}X\text{–}C_5H_4)MCl_2$ (X=CMe_2, $SiMe_2$; M=Zr, Hf) als Metallocenkatalysatoren für die Ethylenpolymerisation. Die Molekülstrukturen von $(C_9H_5CH_2Ph\text{–}CMe_2\text{–}C_5H_4)MCl_2$ (M=Zr, Hf). J Organomet Chem 558: 111-121
10. Alt HG, Jung M (1999) C_2-bridged metallocene dichloride complexes of the types $(C_{13}H_8\text{–}CH_2CHR\text{–}C_9H_6\text{–}nR'n)ZrCl_2$ and $(C_{13}H_8\text{–}CH_2CHR\text{–}C_{13}H_8)MCl_2$ (n=0, 1; R=H, alkenyl; R′=alkenyl, benzyl; M=Zr, Hf) as self-immobilizing catalyst precursors for ethylene polymerization. J Organomet Chem 580: 1-16
11. Alt HG (1999) The heterogenization of homogeneous metallocene catalysts for olefin polymerization. J. Chem. Soc., Dalton Trans: 1703-1710
12. Alt HG (2005) Self-immobilizing catalysts and cocatalysts for olefin polymerization. Dalton Trans: 3271-3276
13. Licht A, Alt HG (2002) Synthesis of novel

metallacyclic zirconocene complexes from ω-alkenyl-functionalized zirconocene dichloride complexes and their use in the α-olefin polymerization. J Organomet Chem 648: 134-148

14. Alt HG (2006) Metallacyclic metallocene complexes as catalysts for olefin polymerization. Coord Chem Rev 250: 2-17
15. Görl C, Alt HG (2007) Iron complexes with ω-alkenyl substituted bis(arylimino) pyridine ligands as catalyst precursors for the oligomerization and polymerization of ethylene. J Mol Cat A Chem 273: 118-132
16. Görl C, Alt HG (2007) The combination of mononuclear metallocene and phenoxyimine complexes to give trinuclear catalysts for the polymerization of ethylene. J Organomet Chem 692: 5727-5753
17. Görl C, Alt HG (2007) Influence of the para-substitution in bis(arylimino)pyridine iron complexes on the catalytic oligomerization and polymerization of ethylene. J Organomet Chem 692:4580-45925
18. Kestel-Jakob A, Alt HG (2007) Boryl-substituted zirconocene dichloride complexes as catalyst precursors for homogeneous ethylene polymerization. Z Naturforsch 62b: 314-322
19. Ostoja Starzewski KHA, Kelly WM, Stumpf A, Freitag D (1999) Donor/acceptor metallocenes: A new structure principle in catalyst design. Angew. Chem Int Ed 38: 2439-2443
20. Ostoja Starzewski KHA (2004) D/A-metallocenes: The new dimension in catalyst design. Macromol Symp 213: 47-56
21. Schilling M, Bal R, Görl C, Alt HG (2007) Heterogeneous catalyst mixtures for the polymerization of ethylene. Polymer 48: 7461-7475
22. Böhmer I, Alt HG (2009) Influence of triphenylphosphine on the activity of heterogeneous iridium, rhodium and platinum containing catalysts for the dehydrogenation of saturated hydrocarbons. J Organomet Chem 694:1001-1010
23. Taubmann S, Alt HG (2008) Catalytic dehydrogenation of cyclooctane in homogeneous solution with titanium, zirconium and hafnium complexes containing N,O-chelating ligands. J Mol Cat A Chem 289: 49-56
24. Alt HG, Denner CE, Taubmann S (2009) "Like Phoenix from the ashes"! Thermally decomposed metallocene complexes as catalysts for CH activation reactions. JJC 4: 45-54