High Mileage Ziegler-Catalysts: Excellent Tools for Polyethylene Production

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SUMMARY: High mileage titanium based Ziegler-catalyst, aluminum alkyl cocatalyst systems are widely used in industry today to produce a broad spectrum of polyethylene grades. The performance of these catalyst systems is excellent because they are well adapted to the technical processes and able to produce an interesting product portfolio. It will be reported how these catalyst systems work, how they are formed, and how they can be utilized in technical processes. These catalyst systems can be regarded as a benchmark for further catalyst developments in industry. Their introduction in industrial processes represents a technological breakthrough.

Introduction

The catalyst or catalyst system plays the key role in all catalytic processes [1)], and this is also and in particular the case for catalytic polymerization processes [2)]. The catalyst together with the cocatalyst aluminum alkyl is the core for the catalytic polymerization of ethylene and 1-olefins as comonomers influencing the polymerization process, the polymer structure and the process performance. Titanium based Ziegler-catalyst, aluminum alkyl cocatalyst systems are well-known and well-approved since a long time[3)], and they have been further improved over years to reach high activity in combination with further needs to drop-in these catalyst systems into existing or new technical processes [4)]. State of the art high mileage catalysts are titanium-based catalysts on magnesium dichloride supports [5,6)].

Ziegler and coworkers [3)] found that catalyst systems for the polymerization of ethylene at low pressures and moderate high temperatures are formed by the combination of precipitated $TiCl_3$ particles and dissolved aluminum alkyls in a hydrocarbon diluent. Cossee and Arlman [7,8)] for the first time presented a reaction model of this catalytic polymerization process, and based on this model some key points could be understood:

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The larger chlorine anions are forming a closest package of spheres and in the voids there are sitting the much smaller titanium cations. Inside the crystal each titanium cation is surrounded by six chlorine anions to form a hexagonal or cubic structure. Regarding the surface a special topology can be seen with an exposed chlorine anion and an exposed titanium cation sitting in the center of 4 chlorine anions. Position 5 is a chlorine in the bulk of the crystal, position 6 is unoccupied and forms a free vacancy.

Starting from this situation all experimental facts can be explained: The activation by the cocatalyst aluminumalkyl takes place by a chlorine alkyl exchange of the exposed chlorine anion to form a Ti-carbon bond. The catalytic cycle is initiated by side-on binding of an olefin - here mainly ethylene - at the titanium. Binding the olefin means at the same time activation of the C,C-double bond for the insertion into the Ti-carbon bond. This insertion runs via a metalla-cyclobutane intermediate. By insertion of the olefin into the Ti-carbon bond the polymer chain has grown by one monomer unit, and at the same time there is again the vacant site at the titanium center to start the next catalytic cycle.

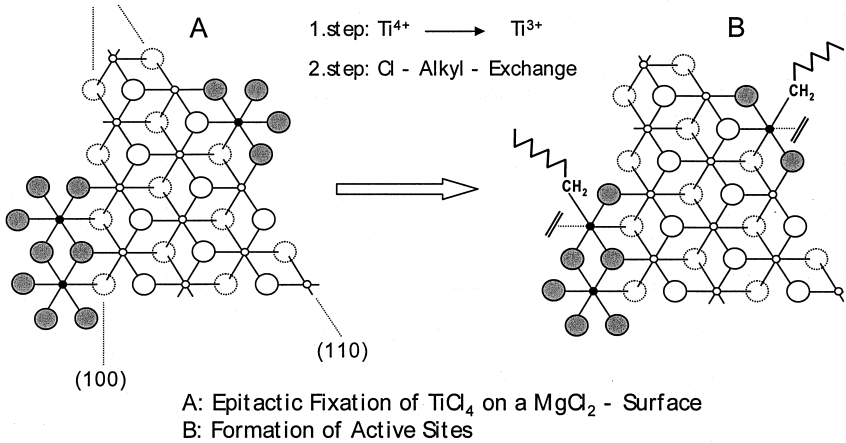
The first generation Ziegler-catalysts were formed by reduction of $TiCl_4$ in a hydrocarbon diluent thus generating a fine $TiCl_3$ precipitate. Only a minor amount of titanium centers at the surface are accessible for polymerization to form active sites. Consequently the mileage of these catalysts in combination with aluminumalkyls as cocatalysts in respect to titanium or $TiCl_3$ was low. The catalyst residues in the polymer were high and have to be destroyed and removed by further steps to reach acceptable final product quality [4].

Formation of High Mileage Ti-based Catalysts

The great breakthrough was achieved finding that $MgCl_2$ is an outstanding support material for titanium-based catalysts. $MgCl_2$ and $TiCl_3$ have the same crystal structure and nearly the same lattice parameters (Table 1). Therefore $TiCl_4$ can be adsorbed and bond at the $MgCl_2$ surface (Fig. 1) [5].

Table 1:

Crystallographic Parameters:	
δ - $MgCl_2$	δ - $TiCl_3$
hexagonal close packed layer structure of Cl^- - Ions	
a = b = 3.63 Å	a = b = 3.54 Å
c = 5.93 Å	c = 5.86 Å
cation coordination : octahedral	
Mg - Cl : 1.23 Å	Ti - Cl : 1.25 Å
Mg^{2+} : 0.65 Å	Ti^{4+} : 0.68 Å
	Ti^{3+} : 0.76 Å



A: Epitactic Fixation of $TiCl_4$ on a $MgCl_2$ - Surface
B: Formation of Active Sites

Fig. 1: Surface Topology of $MgCl_2$-Supported Titanium Catalyst

By treating $MgCl_2$ with $TiCl_4$ titanium can be fixed at the surface. After careful washing and further treatment with aluminum alkyls reduction of Ti^{4+} to Ti^{3+} takes place to form

finally a vacant site at the titanium center. After exchange of a chlorine bound at the titanium by an alkyl group an active site at the surface of the $MgCl_2$ support is built-up having a similar structure as described by Cossee and Arlman for $TiCl_3$ activated with the cocatalyst aluminumalkyl [7,8]. Corradini and coworkers have described this process, meaning that the titanium centers are sitting at the surface of the $MgCl_2$ support to form active sites [9]. From ab initio molecular dynamics structure and chain growth at the titanium centers supported on $MgCl_2$ were described in a different way [10]. But independent of the active site structure and the mechanism of the catalytic process there is a common understanding that the active titanium centers are fixed at the surface of $MgCl_2$ crystals, and that polymerization takes place by an activation of the olefin at the titanium transition metal to be inserted in the Ti-carbon bond.

However, the fixation of the active site at the surface of $MgCl_2$ does not necessarily mean to have a high mileage catalyst. For the formation of high mileage catalysts it is essential to have a highly porous $MgCl_2$ support with a high specific surface. Further it is necessary to shape the average particle size and the particle size distribution. There have been numerous efforts to reach these targets, but nowadays only four different routes are known, approved and used in technical processes to form high mileage $MgCl_2$ supported Ziegler-catalysts.

- Dry milling of $MgCl_2$ together with $TiCl_4$ [11,12].
- Precipitation of $MgCl_2$ dissolved in C_2H_5OH by injecting into a hydrocarbon diluent, and treating with $TiCl_4$ [12,13].
- Forming a $MgCl_2$ support by reaction of dialkyl-Mg-compounds with aliphatic chlorhydrocarbons like $CHCl_3$ in a hydrocarbon diluent, and treating with $TiCl_4$ [14].
- Transformation of suspended Mg-dialkoxides with $TiCl_4$ dissolved in a hydrocarbon diluent to form a $MgCl_2$-titanium catalyst and soluble Ti-tetraalkoxides [15].

All these catalysts are insoluble in hydrocarbon diluents and they are free of soluble Ti-compounds. These procedures lead to catalysts having the targeted average particle size, particle size distribution, particle shape and polymerization behavior.

Polymerization Behavior

These catalysts in combination with aluminum alkyls as cocatalysts fulfill all recommendations to be used in advanced polymerization technologies either slurry or gas phase processes.

In the course of polymerization the catalyst particles are transferred into polymer particles with the targeted average particle size, particle size distribution, particle shape and very important a high bulk density.

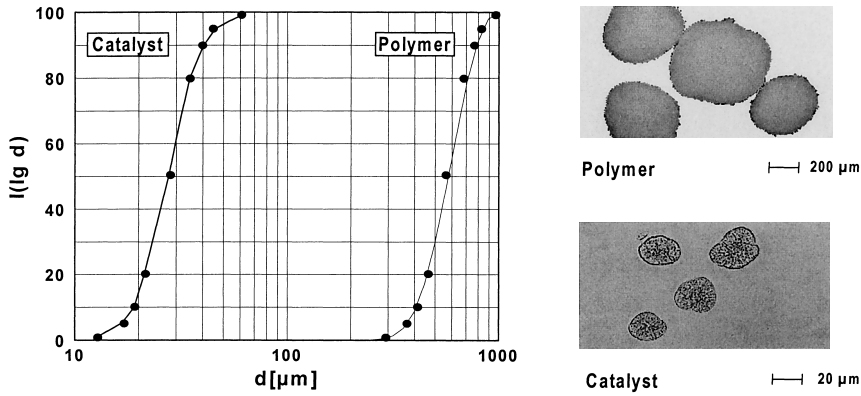


Fig. 2: Spherical Catalyst and Polymer Particles, Particle Size Distribution

This figure shows an increase of average particle size by a factor of 20 to 30, corresponding to an increase in volume of around 10.000. Particle size distribution and particle shape remain the same.

The particle forming process starts from the highly porous catalyst particle which is an agglomerate of much smaller primary particles. When the solid polymer is formed at the surface of these primary particles the polymer disrupts the catalyst particle and the primary particles are evenly distributed over the expanding polymer particle.

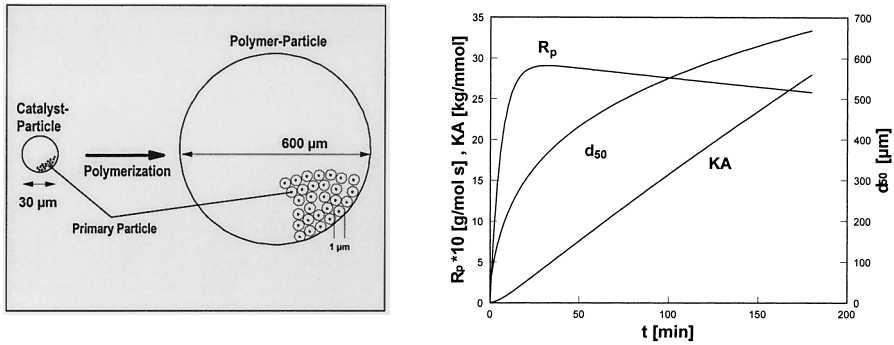


Fig. 3: Particle Forming Process and Polymerization Behavior; R_p: Rate of Polymerisation; KA: Catalyst Productivity; d_{50} Average Particle Size

This type of particle forming process is called polymeric flow model or multigrain model [16,17].

However, the particle forming process only runs in this way if at start-up of polymerization at the virgin catalyst particle the rate of polymerization is low. When the particle expands then the rate of polymerization must increase to reach a high, slowly declining level over a period of time of one average residence time of the polymerization process or beyond. This leads to a high catalyst productivity.
Each polymerizing particle is a very small expanding reactor with its own energy and mass balance called microreactor as described in general by Wicke [18] and for the polymerizing particle elsewhere [17,19].

If a very fast and highly exothermic reaction like polymerization of ethylene takes place inside this microreactor there can be strong ethylene concentration and temperature gradients both inside and at the surface of the particle [19]. The most critical period is the start-up of polymerization when the microreactor and its outer surface is small.

But overheating of the microreactor cannot occur if heat production is always below heat removal via the outer surface as shown on fig. 4.

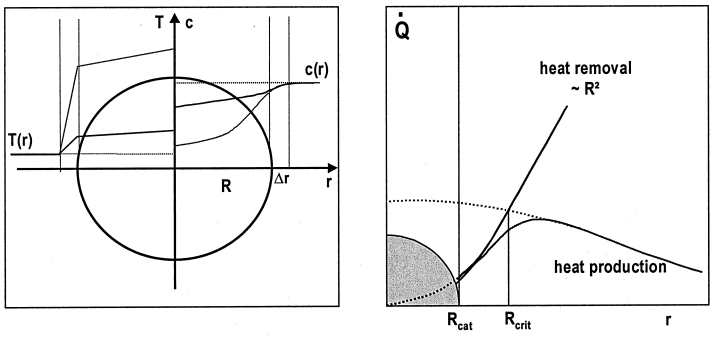


Fig. 4: Microreactor: Polymerizing Particle

Overheating can further be avoided by increasing the microreactor radius up to R_{crit} before polymerization start-up . This can be done by a slow prepolymerization process.

Polymer Properties Control

With these high mileage catalysts a broad spectrum of grades different in average molecular mass, comonomer content, molecular mass distribution and comonomer distribution must be accessible in the technical process. There is a big advantage of these titanium-based catalysts: At a given temperature the average molecular mass can be easily controlled by hydrogen. Average molecular mass or Melt Flow Rate (MFR)[20], is correlated with the hydrogen, ethylene ratio (PH_2/PC_2) in the gas phase of the reactor. But hydrogen reduces activity. Excellent catalysts from a technical point of view are operating at high activities even if high amounts of hydrogen are applied.

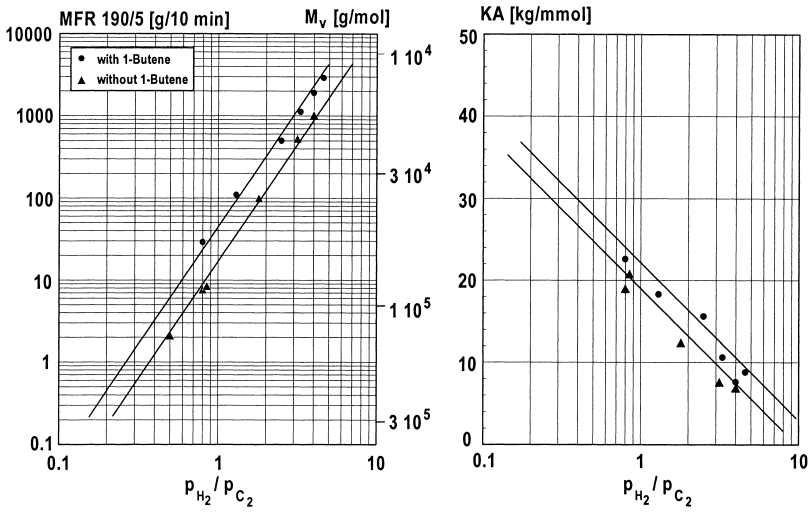


Fig. 5: Molecular Mass Regulation with Hydrogen

From the data given in fig. 5 it can be seen that this catalyst system is able to produce very low molecular mass compounds at still reasonable productivities, and on the other hand it can generate very high molecular mass polyethylene at very low hydrogen, ethylene ratios. This opens the possibility to apply this catalyst system in a cascaded process for PE-HD production with broad bimodal molecular mass distributions. Using these catalyst systems ethylene can be further copolymerized with 1-olefins. However, the Mayo, Lewis parameters are very different which means that only small amounts of the comonomer are incorporated into the copolymer even at high 1-olefin, ethylene ratios in the polymerization reactor. This copolymerization behaviour is not favorable but it does not limit application of these catalyst systems in technical processes.

PE-HD Product Portfolio

A broad spectrum of polyethylene grades mainly in the high density range with outstanding combinations of properties is accessible. By changing the process configuration from a continuous stirred tank reactor to a cascade of two reactors in series, the molecular mass distribution can be widely changed from unimodal with a polydispersity M_w/M_n starting at 5 to bimodal with M_w/M_n-values of 30 and beyond.

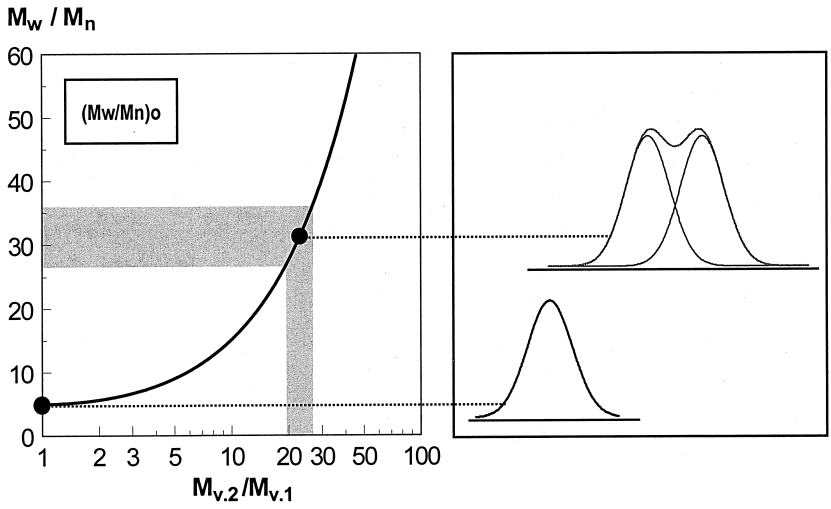


Fig. 6: Polydispersities, Molecular Mass Distributions

This is achieved by variation of the average molecular mass ratio in both reactors. It is further favorable to influence the comonomer distribution by incorporating the co-monomer mainly in the high molecular mass fraction to get outstanding combinations of properties, e.g. for pipe materials [21].

Fig. 7 shows the field of PE-HD products which can be produced using these high mileage catalyst systems

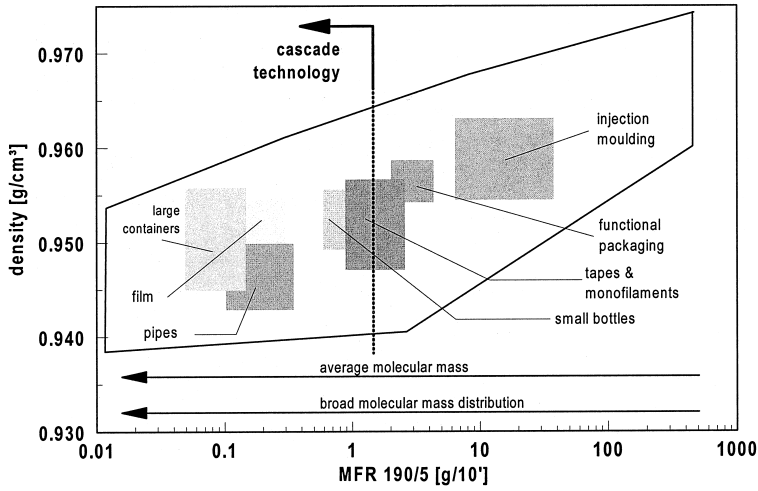


Fig. 7: HD-Product Map

All these products are setting the standards in the PE-HD field for a broad spectrum of applications: pipes, films, textiles, functional packaging and special applications in injection moulding.

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