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Ziegler–Natta Catalysts: Applications in Modern Polymer Science

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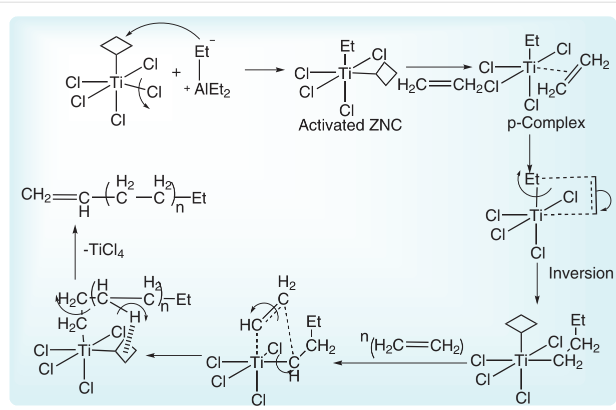
Karl Ziegler, a scientist from Germany, discovered that combining $TiCl_4$ and $Al(C_2H_5)_3$ produced a highly active catalyst that could polymerize ethylene in a stereoregular manner at atmospheric pressure. Later, an Italian chemist named Giulio Natta expanded upon Ziegler's work by developing methods for using the catalyst with other olefins like propylene. Natta also contributed to our understanding of the mechanism behind the polymerization reaction, which led to the development of various forms of the Ziegler catalyst. Over time, scientists have gained more control over stereospecific polymerization thanks to these discoveries.[1–4]

The Ziegler–Natta catalyst is comprised of transition-metal chlorides, including titanium, chromium, vanadium, and zirconium chlorides, that have a distinguished lineage, along with organometallic complexes of triethylaluminium. The crystal structure of the titanium chloride compound contains Ti atoms attached to five chlorine atoms on the surface, with one empty orbital. When the compound reacts with $Al(C_2H_5)_3$, the latter donates an Et group to Ti, causing one chlorine group to detach from Ti.[5–7] This reaction activates the catalyst, as illustrated in Scheme 1, and initiates chain propagation and termination steps, also depicted in the same diagram.

These polymers are useful for manufacturing plastics, fibers, and films. Ziegler and Natta's work on this catalyst earned them the Nobel Prize in Chemistry in 1963.[8,9] The Ziegler–Natta catalysts have undergone several advancements, resulting in four distinct generations of catalysts.

The first generation utilized diethyl aluminum and titanium chloride as co-catalysts. In the second generation of catalysts, titanium chloride/$AlEt_2Cl$ was combined with an internal electron donor, such as ether or ester,[10,11] which enhanced the activity and stereospecificity of the catalysts. The third generation of catalysts was introduced in 1968,[12] and it utilized a catalytic system made up of $TiCl_4$ complexes supported by $MgCl_2$. This method enabled the production of linear polyethylene and isotactic polypropylene. The fourth generation[13,14] of catalysts utilized homogeneous catalysts for conducting olefin polymerizations. Over the years, several noteworthy applications of Ziegler–Natta catalysts have been developed.[8]



Scheme 1 The activation of Ziegler–Natta catalysts (ZNC)

For example, these catalysts have been used to create high-density polyethylene, which is used in products such as bottles and pipes. Additionally, they have been used to create polypropylene, which is used in a wide range of products, including packaging materials and automotive parts.[15,16] Overall, the Ziegler–Natta catalysts have played a significant role in the development of modern polymer science and have contributed to the creation of numerous everyday products.

Table 1 Applications of Zieger–Natta Catalysts

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(A) Yan et al. developed two aminosilane-based external donors, di(piperidyl) dimethoxysilane (DPPDMS) and dipyrrolyldimethoxysilane (DPRDMS), for Ziegler–Natta catalysts used in the homopolymerization of hexene-1 to produce elastomeric polyhexene-1.[17]

Procedure for the Synthesis of External Donors (ED)

DPPDMS

N-Heptane, piperidine, *n*-butyl lithium, and tetramethoxysilane are mixed in a five-neck round-bottom flask at room temperature followed by transferring the resulting liquid to a three-neck round-bottom flask and washing with *n*-heptane. After removing the solvent and unreacted chemicals, a colorless transparent liquid is obtained via low-pressure distillation.

DPRDMS

The kinetic parameters used for the creation of DPPDMS were the same as those employed in this experiment.

Polymerization of Hexene-1

1-Hexene, external donors, and triethylaluminium are combined in a round-bottom flask filled with hexane and stirred while in an environment of nitrogen, water, and little oxygen. After 10 min of 20–50 °C whirling, add tested catalyst. Following a 2 h reaction, add 10% HCl, filter, dry, and weigh the liquid.

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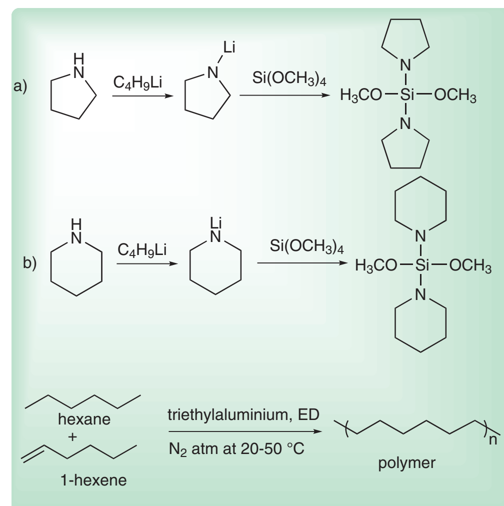

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(B) A new Ziegler–Natta catalyst for polymerization of ethylene and ethylene/1-hexene was produced by Wang and colleagues.[18] The novel catalyst comprises of $(SiO_2/MgO/MgCl_2)\cdot TiCl_x$

Preparation of Catalyst

Dehydrated silica was heated in a fluidized-bed quartz reactor for 2 h, mixed with magnesium acetate solution, and evaporated. The resulting SiO_2/MgO samples were heated and stored. $TiCl_4$ was then added, refluxed, rinsed, and dried to produce a stored fluid powder.

Polymerization of Ethylene and 1-Hexene

During polymerization, a pre-measured catalyst was placed in a 250 mL three-neck round-bottom flask in an oil bath at 70 °C. Ethylene monomer was added to the reactor until the pressure reached 0.12 MPa. Co-catalysts (TEA or TIBA) were added along with *n*-hexane and *n*-heptane, and the solution was saturated with ethylene pressure. Polymerization was carried out for 1 h at 70 °C.

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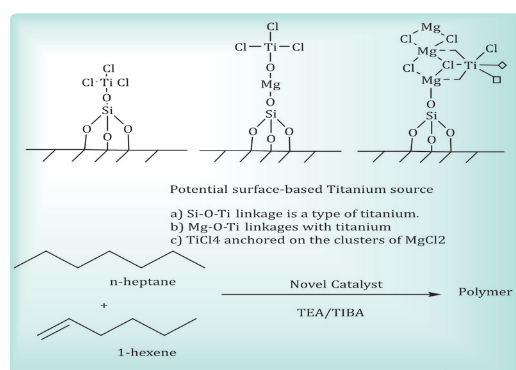

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(C) Tavakoli and team synthesized a bisupported ethoxide-type Ziegler–Natta catalyst composed of $TiCl_4/MCM\text{-}41/MgCl_2$ for in situ polymerization of ethylene.[19]

Preparation of Catalyst

ZME, ZM, and ZE are three types of Ziegler–Natta catalysts. ZME is made by adding magnesium ethoxide with toluene and hexane to preheated MCM-41, followed by addition of $TiCl_4$ and DIBP as an electron donor. After heating and washing with hexane, the ZME catalyst residue is obtained. Two more single-supported catalysts, ZM and ZE, were produced to assess productivity levels.

***In situ* Polymerization of Ethylene**

Polymerization using ethylene and TEA as co-catalyst carried out in a three-neck round-bottom flask on a burner followed by purging of nitrogen gas to ensure inert conditions. Polymerization was initiated by injecting a small amount of catalyst into the reactor containing hexane and co-catalyst at ambient temperature and pressure. The polymerization was stopped by treating with acidified ethanol. The polymer was collected, filtered, and dried at 60 °C under vacuum.[20,21]

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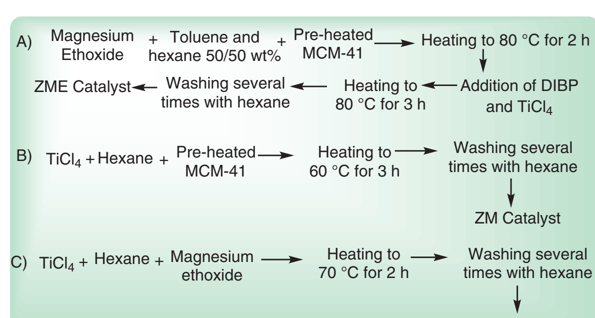

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(D) Meng et al. modified Ziegler–Natta catalysts for ethylene–hexene (E–H) copolymerization using siloxane compounds and internal donors like esters, phosphates, and diethers.[22]

Preparation of Catalyst

Catalyst made in a 250 mL four-neck round-bottom flask with anhydrous $MgCl_2$, *n*-hexane and isobutyl alcohol at room temperature. Internal electron donors 1 and 2 were added, followed by $TiCl_4$ at 70 °C for 2 h. Filtered and washed with *n*-hexene.

Preparation of Copolymer

Copolymer was synthesized at 45 °C in a 250 mL three-neck flask with ethylene, *n*-hexane, 1-hexene, and co-catalyst TEA or TIBA. The reaction was stopped by adding acidified ethanol. The polymer was filtered, washed with ethanol, and dried at 60 °C under vacuum.

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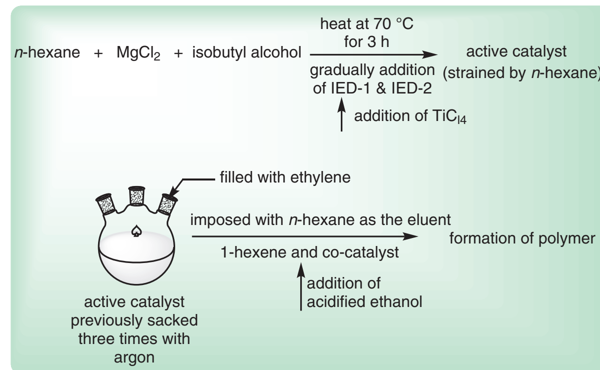

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(E) Recently in 2022, Abazari and coworkers reported a high-performance three-metallic Ziegler–Natta catalyst for ethylene polymerization was synthesized using titanium tetrachloride as the active center, magnesium ethoxide as the support, and ethylaluminum sesquichloride (EASC) as a chlorinating agent.[23]

Preparation of Catalyst

A mixture of diesel oil and magnesium ethoxide was stirred for 8 h at room temperature and then for 10 h at 80 °C. Next, a solution of titanium tetrachloride was added and heated at 110 °C for 1 h, followed by the addition of ethylaluminum sesquichloride and holding at 110 °C for 2 h. The resulting solid catalyst was washed with *n*-hexane and dried.

Preparation of Copolymer

Ethylene was polymerized in a slurry using *n*-hexane as the medium at a pressure of 8 bar. The reactor had a thermocouple, a temperature-control unit, and a mechanical stirrer. The reagents, including TEA, catalyst, and ethylene, were added sequentially at 60 °C, and the reaction was run for 2 h. The reaction was stopped by venting the reactor. Polyethylene samples were then washed, filtered, and dried. The [Al]/[Ti] ratio for the experiment was 714 mol/mol.

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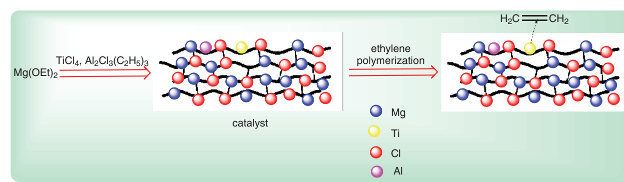

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Conclusion

To conclude, the spotlight article provides an overview of the significance and versatility of Ziegler–Natta catalysts in contemporary polymer science (Table 1). The paper explores the fundamental principles of Ziegler–Natta catalysis, including the activation, insertion, chain propagation, and termination steps involved in the polymerization of olefins. Furthermore, the paper emphasizes the crucial role of Ziegler–Natta catalysts in controlling the stereoregularity of polymers, enabling the synthesis of tailor-made materials with specific properties. With their wide-ranging applications in the production of polyethylene and polypropylene, Ziegler–Natta catalysts continue to drive advancements in materials science, offering opportunities for innovative research and development in various industries.

Conflict of Interest

The authors declare no conflict of interest.

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