Sujet: **Fe-catalyzed Ziegler-Natta-type Polymerization for Polyolefins: From Catalyst to Process**

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Langue de travail : Anglais/Français

Niveau minimum de langue requis :

- Anglais : excellent written anoral (C2)
- Français : not obligatory

Polyolefins extend shelf life, lighten structures and enhance thermal insulation, and are inert chemically. Moreover, they possess the best life-cycle assessment of commodity polymers as of now.[REF] Polyethylene (PE) and polypropylene (PP) thus logically represent almost half of the 350 million tons of global plastics production.[REF as of 2018] Of the different processes used to make polyolefins, the ones implementing Ziegler-Natta (ZN) catalysis are the workhorse of industrial production and responsible for almost 2/3 of all PE and PP (principally *isotactic*-PP) grades synthesized.

At C2P2, we recently discovered a heterogeneous catalytic system based on Iron and inorganic ligands (notably Cl, Mg and B)[REF patents] (akin to conventional Ziegler-Natta systems with Ti), making it possible to (co)polymerize ethylene to reach polyolefins of high molar masses and densities, with an activity comparable to industrial systems based on Ti. The propensity of this iron catalyst to generate very long chains of (co)polymers (from ethylene & ⍰-olefins such as propylene for instance) could be used to design new materials on the basis of a resistant HDPE type skeleton. The extremely linear chains could make it possible to pull PE fibers of high modulus and with unique thermal conductivity comparable to certain metals (Al for example). In addition, the use of less oxophilic Iron could allow for the use of less drastic purity conditions for the process without observing catalyst poisoning. The two advantages of this new iron catalysis are therefore: the linearity and length of the polyolefin chains offering exceptional mechanical properties and the tolerance with respect to impurities. It would thus be possible to manufacture materials based on polyethylene-type fibers UHMWPE (PE featuring ultra-high molar masses) for energy dissipation or based on "polyolefin-based" copolymers for light mechanical reinforcements for infrastructure, or single-material packaging for examples.

From the process viewpoint it is extremely important to relate the process conditions via the catalyst formulation to the final product properties. Parameters such as support size and porosity, catalyst loading, impact of temperature on the productivity and molecular weight distributions, feeding protocols to control the comonomer uptake all play key roles in determining the performance of the catalyst itself. Furthermore, the current catalytic system has been tested only in slurry phase. While slurry phase offers certain advantages such as enhanced heat transfer and thus higher space-time yields in the reactor, gas phase processes offer a number of inherent advantages. These include lower capital and operating costs, easier product separation and recovery, and lower energy consumption.

However the greatest advantage is perhaps the fact that they are swing processes; one can make lower density, lower MW products in a gas phase reactor with far fewer risks of fouling or agglomeration. It is there of great interest to us to see how these potentially significant catalysts behave in the gas phase in order to be able to continue a dialogue with our industrial partners.

Combining the chemistry and process perspectives will significantly enhance the methodology to develop competitive Fe-based Ziegler-Natta processes, potentially transferable to the industry. Our investigation will be focused on identifying the relationship catalyst/process/polymer properties:

We will proceed according several criteria:

- Controlling the (pre)catalyst granulometry (either supported on $MgCl_2$ or $MgCl_2$/Silica)
- Controlling the active-site concentration *via* the variation of [Fe], [B]…
- Exploration of the feasibility of a bi-supported ZN catalyst (mixture Fe, Ti).
- The relationship catalyst size/polymerization control within the process (kinetics…)/polymer thermos-mechanical properties
- Influence of the composition of the gas phase, and in particular of the presence of induced condensing agents (ICA) on catalyst performance