Modifications of Ziegler-Natta Catalysts by Lewis Acids for the Polymerization of Propylene

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Polyethylenes and polypropylenes represent approximately 50wt% of polymers with a fast continuous growth. The “multi-site” character of Ziegler-Natta heterogeneous catalysts (based on TiCl4 supported on MgCl2) has favoured their development with a good compromise between polymer processability of polymers and physical properties and has led them to dominate the manufacture of polyolefins (~50% of polyethylenes and ~100% of polypropylenes) but now it limits the access to polymer ultimate properties which have been made popular by single-site catalysis (e.g. metallocenes). In spite of considerable research efforts the way of operating of these catalysts is far away to be well understood, giving no easy ways to go closer to a single-site behaviour and to surpass the present properties.

From their observed collective behaviour we assumed a new model of active sites based on a “cluster” organization of titanium atoms. This “cluster” hypothesis has led us to investigate simple and versatile treatments of catalysts with Lewis acids (MCln) before the polymerization. Treatments by various Lewis acids of conventional precatblysts evidence various influences of modifications on activity and selectivity or molecular weight distribution depending on the nature of Lewis acid (Figure 1). Following orders can be established: BCl3 >> SnCl4 > SiCl4 >> SbCl5 > GaCl3 regarding activity and SnCl4 ~ SiCl4 >> BCl3 > SbCl5 >> GaCl3 regarding tacticity. The most significant increase of Tm was observed with SnCl4 (Tm = 165.6 °C). Molecular weight distribution can be narrowed using SiCl4, SnCl4 and SbCl5 while it is almost unchanged with other Lewis acids.

Figure 1. Influence of treatments by various Lewis acids on catalyst productivity and selectivity in the propylene polymerization (catalyst: TiCl4 / phthalate / MgCl2 + AlEt3 / silane, T = 70°C, 4 bar propylene, Al/Ti = 250).