

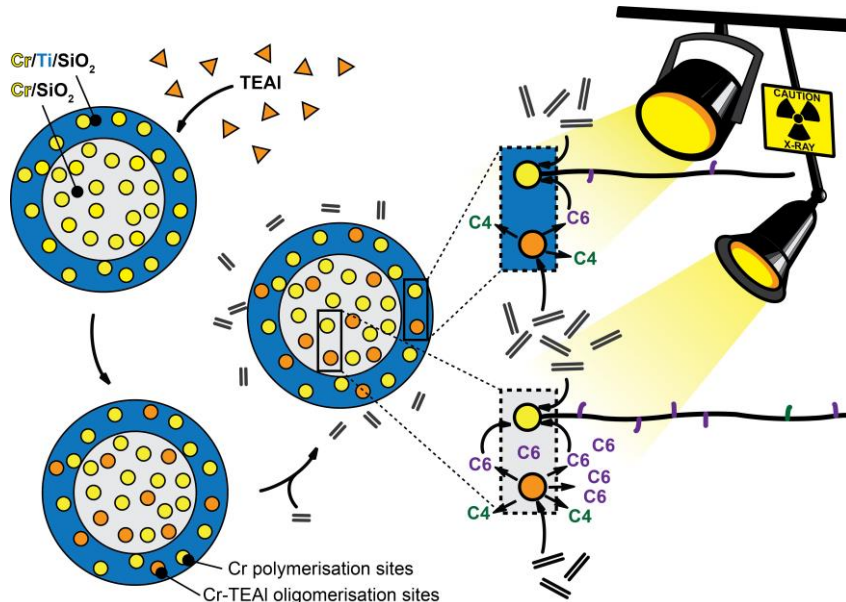
Polyethylene with Reverse Co-monomer Incorporation: From an Industrial Serendipitous Discovery to Fundamental Understanding

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Several years ago at an industrial ethylene polymerisation plant, the *in-situ* generation of co-monomer on a Cr polymerisation line was noted for a Cr/Ti/SiO₂ Phillips-type catalyst. Hence, the co-feeding of 1-hexene was significantly reduced in order to keep a polymer with similar content of co-monomer. The interesting finding was that 1-hexene was the major component, while butene and other oligomers were present in lower concentration. Moreover, the properties of the polyethylene produced were not affected despite the presence of butene. On the contrary, the polymer made even exhibited some improvements. The hypothetical explanation for *in-situ* co-monomer generation was a contamination of the recycling feeds by triethylaluminium (TEAL), as there were several lines with a common recycling section. One of the polymerisation lines was running a Ziegler-Natta catalyst with TEAL as co-catalyst, while the other polymerisation lines ran with a Cr/Ti/SiO₂ catalyst without any co-catalyst.

Pilot and bench scale testing confirmed the *in-situ* co-monomer generation with Cr/Ti/SiO₂ and TEAL. 1-hexene was added in one experiment during the polymerisation when the Cr/Ti/SiO₂ catalyst under investigation was tested without TEAL, as no co-monomer was *in-situ* generated in that particular case. In the second experiment, *in-situ* oligomerisation was induced by modification of the catalyst with TEAL. GPC-IR of the polymers produced clearly shows that less co-monomer was incorporated in the short polyethylene chains than in the long chains when it is generated *in-situ*. Consequently, this so-called reverse co-monomer incorporation is enhanced when the co-monomer is generated *in-situ* in the presence of TEAL. This result came as a positive surprise as more co-monomer incorporated in the high molecular weight fraction of the polymer leads to better mechanical properties.

Based on these initial findings a new type of Phillips-type Cr/Ti/SiO₂ catalyst has been developed, which was prepared from a Cr/SiO₂ pre-catalyst by selective surface-titanation on



the catalyst particle's outer shell and subsequent activation. By pre-contacting the catalyst with TEAL, *in-situ* ethylene oligomerisation sites could be generated. Typically, an olefinic co-monomer (*i.e.*, 1-hexene) is added externally to the reaction mixture and has to diffuse through the growing polymer and catalyst material to arrive at the catalytic sites. We envisioned that it would be advantageous if the co-monomer was generated on the TEAL-

modified active sites within the Ti-scarce catalyst particle close to the active sites that make a high molecular weight polymer. Therefore, *in-situ* produced olefins (*e.g.*, 1-hexene) would be incorporated into longer polyethylene chains. This is illustrated in the schematic of this abstract. Scanning Transmission X-ray Microscopy (STXM) allowed relating these macroscale polymer properties to nanoscale details of individual Cr/Ti/SiO₂ catalyst particles.

More details on this research work can be found in the following reference:

D. Cicmil, J. Meeuwissen, A. Vantomme, J. Wang, I.K. van Ravenhorst, H.E. van der Bij, A. Munoz-Murillo, B.M. Weckhuysen, *Angew. Chem. Int. Ed.* 2015, **54**, 13073-13079.