Titanium Surface Sites in Ziegler-Natta Pre-Catalysts from $^{47/49}$Ti solid-state NMR Signatures

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The initial development of the heterogenous Ziegler-Natta (ZN) polymerization catalyst dates back to the mid-1950s[1]. Despite the industrial importance of the ZN catalysts towards the world production of polyethylene (HDPE & LLDPE) and polypropylene (iso-PP)[2,3], the structure-activity relation until now remains elusive. As a result, decades of development targeted towards performance gains of the highly complex heterogenous catalytic system were primally empirical. In the 1970s, the usage of magnesium chloride ($MgCl_2$) as support of the active site was found to significantly enhance the activity of Ti-based ZN catalysts[2]. However, in order to promote a more rational catalyst design, a detailed molecular-level understanding of Ti surface sites of the ZN pre-catalyst, $TiCl_4/MgCl_2$, which is known to form active sites under polymerisation conditions, is required.

For the evaluation of the Ti surface sites, we turned to $^{47/49}$Ti NMR, which is highly sensitive towards the ligand environment of Ti, altering the local charge distribution and electronic structure. The applications of $^{47/49}$Ti NMR are nonetheless often limited, due to (i) low Ti content in the catalyst (ca. 2 wt%), (ii) the low natural abundance of the NMR nuclei (< 10 %), (iii) the presence of two NMR active isotopes with small resonant frequency difference ($\Delta\delta_{47/49Ti}$ = 267 ppm) and (iv) the quadrupolar nature of both isotopes. In this work, we addressed these challenges by (i) combining high magnetic field (900 MHz), fast magic angle spinning (MAS) and low temperature (100 K) $^{47/49}$Ti NMR measurements, in order to decrease the linewidth and increase sensitivity, (ii) performing state-of-the-art density-functional theory (DFT) computations, and (iii) using BCl_3-treated ZN pre-catalyst[3], which was expected to contain fully chlorinated Ti species, hence a more symmetric electric charge distribution around Ti, associated with more favourable NMR properties, and shown to increase the amount of the active sites.[4] The obtained NMR spectroscopic signatures of Ti surface sites of the ZN catalyst and the application of DFT modelling allowed us to resolve the structure of $TiCl_4$ on $MgCl_2$, a representative industrial pre-catalyst. Analysis of chemical shift and quadrupolar coupling constant helped to highlight the influence of the local environment and $MgCl_2$ morphology on the electronic structure of the Ti sites.

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