

Abstract

The steric and the electronic environment are the fundamental parameters that define the catalytic properties of any active site. For late transition metal catalysts, they determine polymer molecular weight and branching in ethylene polymerization as well as in the ethylene-CO copolymerization, and consequently the final properties of the resulting materials. Among the late transition metal catalysts active in the ethylene polymerization, an interesting class of compounds is represented by Ni(II) salicylaldiminato complexes. Moreover, more recently Ni(II) phosphine phenolate complexes revealed to be interesting for both ethylene polymerization and ethylene-CO copolymerization reactions.

For salicylaldiminato complexes, although a rather conclusive picture on the importance of substituents bulk that already exists, designing the target active site was still a challenge. To this end, a defined steric environment of the active site and the controlled manipulating of the electronic properties for new emerging catalytic systems is essential for a complete understanding of the catalysts' behaviour.

For salicylaldiminato complexes, these aims were achieved:

- by means of the introduction of a further ancillary imine donor that serves also as an additional binding site;
- through the incorporation of a bridging proton $N\cdots H^+\cdots O$ between the two binding sites;
- by means of a cage around the metal centre.

The resulting catalysts proved to be promising candidates to obtain products whose microstructure is strictly dependent on the catalyst structure, ranging from high- molecular-weight polyethylene to oligomers.

For the Ni(II) phosphine phenolate complexes, the same issues were addressed:

- by means of the introduction of a bis-phenyl substituent on the ancillary ligand that provides a suitable and modulable steric and electronic contribution;
- through different nature of remote substituents on the bis-phenyl moiety.

These complexes in addition to being promising candidates to obtain polyethylene-based products with different microstructures, proved to have a peculiar structure. It favours the formation of in-chain-functionalized polyethylenes with a desirable property profile (i.e. low content of CO) for the unique ethylene-CO co-polymerization reaction.

The aims of this thesis were reached by means of quantum mechanical DFT (Density Functional Theory) calculations and by a close collaboration with the experimental group of Prof. Stefan Mecking at the University of Konstanz, which provided the synthesis and characterization of catalysts and of polymerization reactions.