Unraveling the Mechanism of Sustainable Iron Based Oligo – and Polymerization Catalyst Using a Freeze Quench XAS Methodology.

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1. Introduction

It is commonly accepted that the use of aluminum activators (preferably methylalumoxane) in large excess is a key additive in ethene oligo – and polymerization reactions. Although good iron catalysts for these processes are known, the exact mechanism and corresponding oxidation state of the iron species remain under discussion. Activation studies with different aluminum reagents have been conducted using ^{1}H-NMR, transient absorption UV-Vis and freeze quench X-ray absorption spectroscopy (XAS).

2. Experimental methods

All air-sensitive materials were manipulated using standard Schlenk techniques or by the use of a glovebox. All precursors (synthesized according to literature) are activated with aluminum reagents (~300 eq.) and quenched in liquid nitrogen at several points in time. Additional activation experiments were conducted in an ethene atmosphere (1bar).

Fe K-Edge (7112 eV) X-ray absorption measurements were performed at beamline B18 sited of the Diamond Light source (Didcot, UK) and at BM26A (DUBBLE) of the ESRF, using a Si (111) crystal monochromator and a Germanium 36 or 9 element detector. 5mM solutions (toluene) were measured in fluorescence mode. Samples were prepared in kapton tubes and subsequently frozen in liquid nitrogen under argon atmosphere, the samples were kept frozen using a cryo-jet (100K) setup.

3. Results and discussion

The rate of oligo and polymerization showed to be most active with MAO compared to TMA. The use of Isopropyl substituents on the bis(imino)pyridine ligand showed selective dimerization under constant ethylene pressure and 1-octene formation with limited amount of ethylene, according to GC-MS and ^{1}H-NMR. The use of more sterically hindering mesityl substituents on the ligand backbone, show the formation of polyethylene. Time resolved UV-Vis spectroscopy showed the formation of activated species on a millisecond time scale in both cases. Detailed XAS analysis showed the formation of ion pair $[(^{Mes}PDI)Fe(\mu\text{-}Me_2)AlMe_2][MeMAO]$ species. The propagating species are investigated by low temperature ^{1}H-NMR measurements and show the coordination of ethene, most likely represented as $[(^{Mes}PDI)Fe(C_2H_4)Me][MeMAO]$ which was the identified species by detailed EXAFS analysis. TD-DFT and FEFF calculations clarify the observed shifts in the XANES region by looking at the structural and electronic parameters of the precursor, activated - and ethene coordinated species.

4. Conclusions

These results provide strong evidence of the formation of ionic Fe^{II} species at the activation with excess aluminum reagents. The characterization of ethene coordinated species help in understanding the overall reaction mechanism. The difference in oligomerization and polymerization can be attributed to the steric bulk around the reactive centre.

5. Acknowledgements

We wish to thank NWO for funding this project (number: 723.014.010).and Diamond Light Source Ltd. and the ESRF for access to the synchrotron facilities, and the staff at B18 and BM26A for their assistance.