CYCLE DE CONFÉRENCES DE CHIMIE

Avec le concours de : Université Clermont Auvergne
SIGMA Clermont
Ecole Doctorale des Sciences Fondamentales de l'UCA
Société Chimique de France, Section Auvergne

Jeudi 14 février à 15 h

Amphi Rémi (site des Cézeaux)

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Understanding Iron Catalysis to design high-performance Polymers & Copolymers from α-olefins & 1,3-diene

Harnessing sustainable catalysis has become a major workhorse of innovation in Chemistry. Iron is the most abundant transition metal in the Earth's crust. Its high availability and low toxicity render it extremely attractive as a target for metal-based catalytic platforms. Interestingly for polymer chemists, well-defined molecular iron precatalysts provide the opportunity to also control selectivity through monomer selection/coordination/insertion when appropriately choosing the mode of activation. In our project, **iron catalysis** has proven particularly efficient in providing methods to both synthesize polyolefins from ethylene and α-olefins and polydienes from 1,3-dienes.1-4 On the heterogeneous side, the combination of ferrous chloride on exfoliated MgCl2 with appropriate Lewis bases and acids provides an excellent **Fe**-Ziegler-Natta-type precatalyst, which once activated/alkylated displays activities on a par with Ti. On the homogeneous side, redox-active ligands such as iminopyridine- and bisimine-type bidendates confer unique reactivity to the iron centers, affording various oxidation states, as evidenced by Mössbauer and NMR spectroscopies.3-5 By adjusting sterics and electronics, excellent regioselectivity and stereoselectivity have been achieved in the production of polydiene-based elastomers.3,4 Very recently, the concept has been extended to the copolymerization of ethylene with 1,3-dienes.5 Using an advantageous catalyst switch and favorable Fe-Al transmetalations/chain-shuttling processes, and adjusting the ligand set, we were able to achieve **random and/or block-copolymer** structures from ethylene and other 1,3-dienes. Extensive NMR characterizations evidenced the novel structures. These copolymers display unique and valuable physical & mechanical properties, which was shown using DSC & rheology.5 The low cost, low toxicity, low catalyst loading, and high turnover frequency of the catalysts presented could translate, with appropriate development, into industrially relevant processes.

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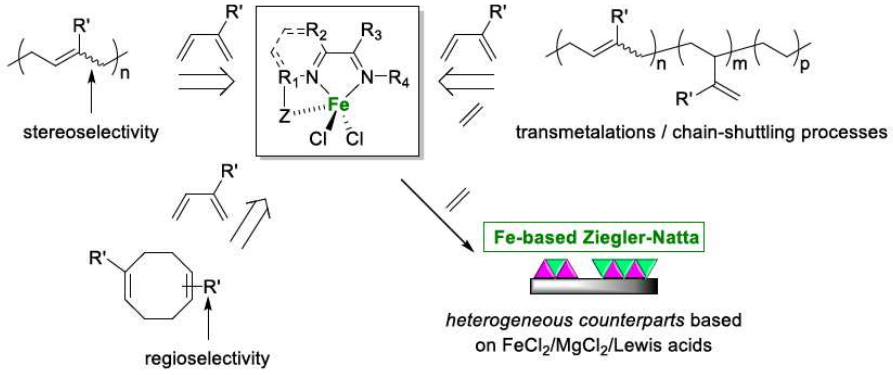

Keywords: Iron Catalysis, Ethylene, 1,3-Dienes, Stereoselective Polymerization, Ethylene/1,3-Diene Copolymerization

References

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3. “Iron-catalyzed polymerization of isoprene and other 1,3-dienes” J. Raynaud, J. Y. Wu, T. Ritter *Angew. Chem. Int. Ed.* **2012**, *51*, 11805 & 12920
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