UniTO - PROPOSAL PhD programme in Chemistry and Material Sciences

Scientific Project Proposal

The PhD program will be part of a long term project devoted to the development of heterogeneous catalysts that convert chemicals, in mild conditions, at high yields and turn-over rates, yet with high specificities and selectivities.

State-of-the-art and objectives

C-C multiple bonds (C=C and C≡C) have a central position in catalysis, and serve as the starting point for making new C-C, C-O, or C-H bonds through oxidative and reductive processes. Ethylene is a versatile C2 building block for the chemical industry and is readily available from fossil and biomass sources. The project will focus on 1) ethylene oligomerization (forming alpha olefins) and 2) alpha olefin hydroformylation (forming aldehydes), two processes which are of considerable academic and industrial interest. The C=C double bond in ethylene is electron rich, and is prone to attack by electrophiles. The simplest electrophiles are acids, but the acid-catalysed transformation of ethylene often suffers from poor selectivity. Alternatively, ethylene may be activated by coordination to transition metal centres, leading to more selective transformations. Ethylene oligomerisation provides linear alpha olefins [1], used as co-monomers in the production of polyethylene and are important building blocks in the synthesis of detergents, lubricants, and surfactants. The hydroformylation of alpha olefins with CO and H₂ leads to the formation of aldehydes with one more carbon than the reacting olefin [2]. These aldehydes can be further hydrogenated to their corresponding alcohols. Selectivity is a major issue in both ethylene oligomerization and olefin hydroformylation. Industrial linear alpha olefin processes mainly employ a combination of alkylaluminum and transition metal (Ni, Ti, Zr) complexes as catalysts, and produce olefins in the C4 to C20+ range. [3] Selective production of C4 to C8 olefins can be achieved with Ti and Cr complexes. [4] Hydroformylation of olefins is catalysed with Co or Rh complexes, and yields a mixture of linear and branched aldehydes. Linear aldehydes typically have greater commercial value than their branched analogous. [2]

Methodology and work plan.

The major challenge that will be addressed will be to develop more robust and selective heterogeneous catalysts where the activity and tunability that is offered by the homogeneous catalysts is retained, or preferably improved. Viable strategies to be explored in the project will involve attachment of organometallic complexes to high surface area porous solids, following supramolecular chemistry concepts (recently applied in hydroformylation reactions [5]) and to modify existing heterogeneous catalysts through appropriate choices of metal-ligand and metal-activator combinations. Ethylene oligomerization and olefin hydroformylation are complex, multi-step processes which involve the cleavage and formation of a large number of bonds. The catalytic sites undergo oxidation state changes and are bonded to ligands that undergo dynamic changes during the reactions; the nature of catalytic intermediates thus need be scrutinized by a broad platform of experimental methodologies. Studies of active sites for oligomerization and hydroformylation with solid catalysts will require adaptations of existing methods. In particular, techniques must be developed to spectroscopically characterize catalytic sites in solid catalysts that are suspended in solvent.

References


Contacts

Professor Silvia Bordiga and Elena Groppo.