ABSTRACT

At the current rate of consumption of petroleum resources, they are predicted to be exhausted within the next century. For this reason, the development of new chemical processes using biorenewable resources is attracting an increasing interest. One of such resource is carbon dioxide: an abundant, nonflammable, non-toxic and renewable carbon source, the only feedstock readily and cheaply available. However, CO_2 has a high thermodynamic stability and many scientists have been and are searching catalysts which overcome the low CO_2 reactivity. In industrially practicable processes, carbon dioxide has to be reacted with energy-rich strained rings. In particular, the transformation of epoxides and carbon dioxide into either cyclic carbonates or aliphatic polycarbonates is one of the most attractive and commercially important process.

Since the discovery of catalysts for the coupling of CO_2 and epoxides in the late 1960-s, a significant amount of research has been directed towards the development of catalysts with improved activity and selectivity. In the first chapter, well-defined catalysts for CO_2/ epoxide reactions are described, with particular enphasis to catalysts deriving from inexpensive, earth-crust abundant metals, such as aluminum, zinc and iron.

In the second chapter, the synthesis of monometallic salalen aluminium complexes and their use as catalysts in the reactions of CO_2 with different epoxides is described. In particular, the reaction of cyclohexene oxide and CO_2 was thoroughly investigated. The effect of the reaction conditions (nature and equivalents of the cocatalyst, CO_2 pressure and temperature) and of the ligand structures (substituents on the ancillary ligand, nature of the labile ligand and nature of the nitrogen donor atoms) on activity and selectivity of the catalysts was studied. Moreover, the cycloaddition reaction of the CO_2 with terminal epoxides, bearing different functional groups, was realized. Finally, NMR mechanistic studies have been carried out to shed light on the catalytic cycle active with this class of catalysts. Interestingly, the characterization of an intermediate species in the mechanism of the reaction of cyclohexene oxide with CO_2, catalyzed by one of the salalen–aluminum complexes, was accomplished.

In the third chapter, the synthesis of an iron complex with one of the salalan ligands used for aluminium complexes and its counterparts, salen and salan ligands, is described. The ligands bear the same substituents on the phenolate rings and differ only for the nature of the nitrogen donor atoms. The paramagnetic iron complexes were characterized by UV-Vis and IR-spectroscopy, MALDI-ToF mass spectrometry and measurement of magnetic moments by the NMR Evans method. The catalytic behaviour of these systems in the reaction of CO_2 with benchmark epoxides, such as propylene-oxide (PO), styrene-oxide (SO) and cyclohexene-oxide (CHO) and subsequently in the ring-opening polymerization of L-lactide and ε-caprolactone was investigated.

In the fourth chapter the synthetic strategy conceived for the preparation of a new class of hexadentate ligands is described. These ligands present two additional sulphur donors between the phenolate moieties and the imino atoms of the classic salen ligands, thus creating a coordinative environment able to allocate two metal centers. The first ligand of this class has been synthesized and then used for the preparation of the corresponding bimetallic Zn (II) complex. The zinc complex has been tested in the reaction of CO_2 with cyclohexene oxide. The effect of the reaction conditions (such as, temperature, CO_2 pressure and time) on the activity and the selectivity of the catalyst was evaluated.

In the fifth chapter of this thesis, an organocatalytic approach towards the synthesis of highly substituted cyclic carbonates from tri- and tetra-substituted epoxides and carbon dioxide is described. The developed protocol involves the use of a simple base under mild conditions towards the initial formation of a less substituted carbonate product. The latter equilibrates to a tri- or even tetra-substituted cyclic carbonate under thermodynamic control and can be easily trapped *in situ* providing overall a new domino process for the preparation of synthetically elusive heterocyclic scaffolds.