

**The interaction of CO₂ with amines
as molecular control factor
in catalytic processes**

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH
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Parts of this thesis have already been published:

- *Controlling reaction selectivity through reversible ionic liquids*, I. M. de Wispelaere, G. Franciò, W. Leitner, *Poster*, 44. Jahrestreffen Deutscher Katalytiker mit Jahrestreffen Reaktionstechnik, Weimar, **2011**.
- *Rhodium catalysed selective hydrogenation of dienes to monoenes in reversible ionic liquid solvents*, I. M. de Wispelaere, K. Wittmann, G. Franciò, W. Leitner, *Poster*, 4th International IUPAC Conference on Green Chemistry, Foz do Iguaçu, **2012**.
- *Stereoselective synthesis of cyclic carbonates from oleo-chemicals and CO₂ using reversible ionic liquids and organic halides*, I. M. de Wispelaere, J. Langanke, G. Franciò, W. Leitner, *Poster*, 4th International IUPAC Conference on Green Chemistry, Foz do Iguaçu, **2012**.
- *Rhodium catalysed selective hydrogenation of dienes to monoenes in reversible ionic liquid solvents*, I. M. de Wispelaere, K. Wittmann, G. Franciò, W. Leitner, *Poster*, Green Solvents for Synthesis, Boppard, **2012**.
- *Comprehensive monitoring of a biphasic switchable solvent synthesis*, S. Hardy, I. M. de Wispelaere, W. Leitner, M. A. Liauw, *Analyst* **2013**, *138*, 819–824.

Abstract

The present thesis deals with the interaction of CO₂ and amines as molecular control factor to influence different kinds of selectivities in various catalytic processes. The reversibility of the Lewis acid-base reaction between CO₂ and amines has been applied in numerous reaction and separation processes and chapter I gives a short overview of the different areas.

Up to date this interaction has not been used to steer the selectivity of a reaction and in this context, switchable solvents are applied in the selective homogeneous hydrogenation to steer the chemoselectivity in chapter II. The interaction between CO₂ and amine was ensured by using the switchable solvent system of DBU and 1-hexanol. This switchable solvent system was characterised in detail in order to obtain a deeper insight on its effects in the reaction. Different homogeneous rhodium-complexes were evaluated as catalysts in the selective hydrogenation of 1,3-cyclohexadiene and 1,4-cyclohexadiene and the presence of various bases on the selectivity towards cyclohexene was investigated. As a result, the rhodium-complex [Rh(cod)(dppp)]BF₄ was selected for further studies including concentration profiles, mechanistic considerations and catalyst recycling in the switchable solvent system.

In chapter III, switchable ligands for the control of coordination geometries in catalysis are discussed. These ligands are guanidine substituted triphenylphosphines, which can interact with CO₂ in presence of an alcohol. The synthesis of these ligands is described and the interaction between the ligands, 1-hexanol and CO₂ is investigated using high-pressure NMR spectroscopy. The largest interaction was found between the *meta*-substituted ligand. The influence of the switchable ligands on the regioselectivity in the rhodium-catalysed hydroformylation of 1-octene was tested, where the influence of the substituted position (*ortho*, *meta* or *para*) and different alcohols on the selectivity were evaluated.

In chapter IV, switchable catalysts were used for the synthesis of cyclic carbonates derived from styrene oxide and epoxy derivatives from oleo origin. The reaction of styrene oxide with CO₂ in presence of switchable catalysts based on DBU and 1-hexanol was tested and an optimisation of the reaction conditions was performed. To investigate the influence of the catalysts on the stereoselectivity, the conversion of different epoxy oleo chemicals into cyclic carbonates with simple halide catalysts and switchable catalysts was tested. A clear switch in the product distribution of *cis*- and *trans*-cyclic carbonates could be observed with the different catalysts. A detailed evaluation - including mechanistic and stereochemical considerations - was done.

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