Doctoral thesis:

A study on the catalytic performance of acidic ionic liquids in model chemical processes

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Designing of a new and sustainable protocols for many organic reactions are becoming increasingly important. Next to the economic efforts, ecological aspects of the process are also taken into account. Particular attention is paid to optimizing the production methods of fine chemicals group compounds which is often multi-stage and involve the production of large quantities of by-products. The main challenges for the production methods are the elimination of Volatile Organic Compounds (VOCs) and the search for highly active catalyst which allows to reduce the temperature, reaction time and, above all, increase of efficiency and selectivity.

The aim of these study was to develop acidic ionic liquids which will serve as highly active catalysts. Ionic liquids can be design to carry a desired properties *eg.* by introducing an acidic function into the cation or anion structure. They may contain Lewis or Brønsted acidic centres. Lewis acidic ionic liquids have an metal (M) with free or not fully occupied orbital, capable of accepting electrons. These compounds are classified to the group of halometallic ionic liquids. On the other hand, the presence of a labile proton in the cation (protic ionic liquids) or anion, which can then act as a proton donor, makes it a Brønsted acidic.

Followed by this guidelines concerning exploration of a new, highly active and non-toxic catalyst, four new catalytic systems were design during this work, which were used in three model reaction: Fisher esterification, Diels-Alder cycloaddition and Friedel-Crafts alkylation (Table 1). These catalyst exhibit Brønsted or Lewis properties and form homo- or heterogeneous reaction systems.

Particularly, the following catalyst were used in this work:

- protic ionic liquids based on aliphatic and aromatic amines and sulfuric acid,
- chlorometallate ionic liquids build from dialkylimidazolium cation and chlormetallate anions (where metal M = Al(III) and Ga(III)) immobilised on the mesoporous silica support with multimodal structure,
- borenium ionic liquids based on borenium cation and chlorometallate anions ((where metal M = Al(III) and Ga(III))
- liquid coordination complexes basen on amines and phosphines as ligands and $GaCl_3$.

Table 1. New developed catalysts in this work and their application in model chemical processes.

No.	Catalyst (abbreviation)	Acidic centre	Reaction	Reaction system
1	Protic ionic liquids based on H_2SO_4 (PILs)	Brønsted	Fischer esterification	Heterogeneous (biphasic) with liquid catalyst
2	Chlorometallate ionic liquids immobilised on silica surface	Lewis	Dielsa-Alder cycloaddition	Heterogeneous (biphasic) with solid catalyst
3	Borenium ionic liquids (BILs)	Lewis	Dielsa-Alder Cycloaddition	Homogeneous
4	Liquid coordination complexes based on $GaCl_3$ (LCCs)	Lewis	Friedel-Crafts alkylation	Homogeneous

Ionic liquids used in this study have divers Lewis and Brønsted acidic properties in rage of AN = 66 – 182. All catalysts obtained and used in this work showed high activity in the studied processes.

As a result of dissertation, one review paper and four publications describing the results of the research have been published.