

Ionic liquids – application driven synthesis in green chemistry

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Abstract – Ionic liquid-based strategies are presented as a generic approach to tailoring catalysts as a replacement of hazardous acids in industrially-relevant reactions, to generate both environmentally and economically sustainable processes. The possibilities of application of new Brønsted and Lewis acidic ionic liquids as catalysts, mainly in the synthesis of fine chemicals: lactones, amides, esters, Diels-Alder cycloadducts and alkylbenzenes are presented.

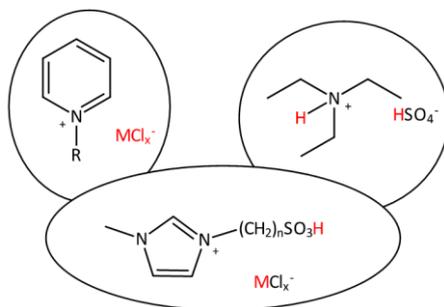
Keywords – acidic ionic liquids, fine chemicals, green chemistry, oxidation, esterification.

Introduction

Searching for new, highly specialized catalysts is a challenge facing modern industry. They are required for the design of clean, environmentally friendly technologies dedicated to the chemical industry. Acidic ionic liquids make promising alternatives to conventional acids for catalysis, and lead to a both greener and economically viable process. In this contribution, various approaches to implementing Brønsted and Lewis acidic ionic liquids as solvents and catalysts in various chemical reactions are discussed. Both homogenous and heterogeneous systems are proposed. Ionic liquids presented in this study are known as "tailor-made." This means that for a specific application, the required catalyst properties can be determined based on an optimal structure by selecting the appropriate reagents for its synthesis.

Results and Discussion

Acidic ionic liquids are salts that may have an acidity centre located in the cation or anion. Examples of acidic ionic liquids structures are presented in Scheme 1.

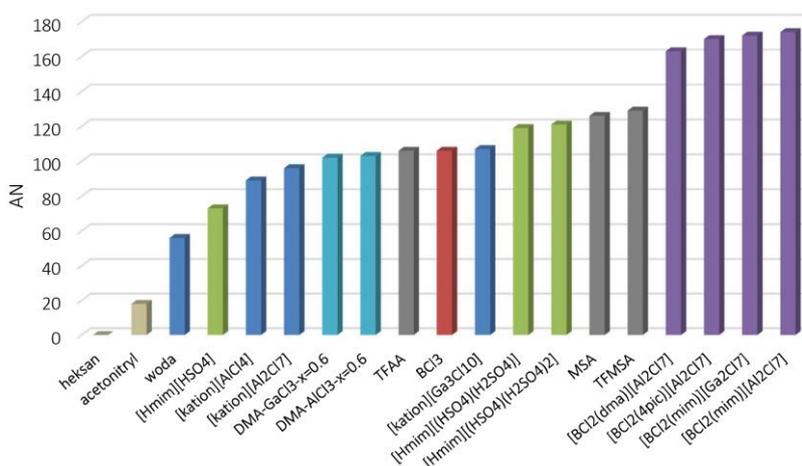


Scheme 1. Acidic ionic liquids with Lewis, Brønsted or both acidity (where M is metal).

The new catalytic systems proposed in this subject include the following:

- protonic ionic liquids based on aliphatic and aromatic amines and sulfuric acid,¹
- chlorometallate ionic liquids made from dialkylimidazolium cation and chlorometallate anions (metal: Al(III) or Ga(III)), also immobilized on the surface of a mesoporous silica material with a hierarchical pore structure,^{2,3}
- borenium ionic liquids based on borenium cation and chlorometallate anions (metal: Al(III), Ga(III)),⁴ and
- liquid coordination complexes based on selected amines and phosphines and GaCl₃.⁵

Studied catalysts were characterized by spectroscopic methods and their Gutmann Acceptor Numbers (AN) were determined. Thanks to these studies, all acidic ionic liquids, i.e., with properties of both Brønsted and Lewis acids, can be compared and sorted with increasing acidity (Scheme 2).



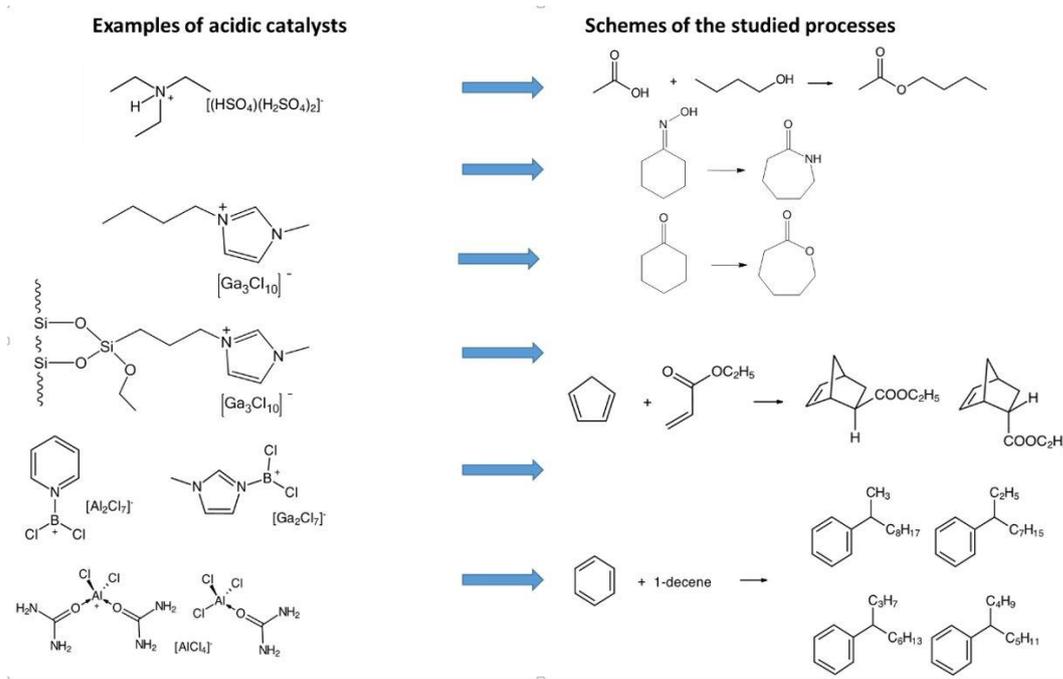
Scheme 2. Comparison of AN for ionic liquids (green – protonic ionic liquids, purple – borenium ionic liquids) and liquid coordination complexes (turquoise) with literature data (abbreviations: TFAA - trifluoroacetic acid, MSA - methanesulfonic acid, TFMSA - trifluoromethanesulfonic acid, [Hmim]⁺ - 1-methylimidazolium cation, DMA – N,N- dimethylacetamide).

The determination of AN has enabled the placement of new acidic ionic liquids in a number of acidic catalysis. The rapid selection of suitable acidic catalysis with appropriate acidity for the reaction is now possible. Borenium ionic liquids exhibit very high acidity, and the highest ever recorded was AN \approx 182. They are superacids with acidity centres located in both borenium cations and chlorometallate anions. Protonic ionic liquids with a composition $\chi_{\text{H}_2\text{SO}_4} = 0.75$ show a strong acidic nature (AN \approx 121) that is close to methanesulfonic acid (AN = 126.1) and higher than trifluoroacetic acid (AN = 105.5).

Notably, the catalysis were used in homo- or heterogeneous systems. Protonic ionic liquids based on sulfuric acid that were used in the esterification reaction formed a heterogeneous two-phase system with a liquid catalyst. Chlorometallate ionic liquids immobilized on the silica surface used for the Diels-Alder reaction are also examples of heterogeneous catalysis. Borenium ionic liquids in Diels-Alder cycloaddition and chlorometallate ionic liquids in Baeyer-Villiger reaction ensured the homogeneity of the reaction system; similar action was shown with liquid coordination complexes in the Friedel-Crafts alkylation.

To summarize, all of the newly developed ionic liquids were highly active acidic catalysis. Protonic ionic liquids based on sulfuric acid showed significantly higher catalytic activity in the esterification and Beckmann rearrangement reaction than previously described in the literature ionic liquids. Borenium ionic liquids have shown the highest catalytic activity in the Diels-Alder reaction among all systems studied to date. The cost of the synthesis of such a catalyst is high, and the catalyst is consumed during the reaction, but its high cost can be compensated by the very low amount necessary for the reaction. Chlorometallate ionic liquids, also in the form immobilized on a silica surface, exhibit high catalytic activity in Baeyer-Villiger and Diels-Alder reactions. The liquid coordination complexes used in the alkylation of benzene with 1-decene exhibit better results compared to industrial processes and chlorometallate ionic liquids.

All the catalysis listed above are acidic ionic liquids, except the GaCl₃-based liquid coordination complexes, which have similar properties to ionic liquids. Spectroscopic studies have shown that they are composed of a mixture of cations, anions and molecules in dynamic balance. Hence, they cannot be completely classified as a group of ionic liquids, which, by definition, are built exclusively from ions.



Scheme 3. Examples of acidic catalysts and their use in the selected reactions.

Conclusion

The ability to select acidity from a rich palette of ionic liquids with Brønsted and/or Lewis properties, a lack of vapour pressure, the ability to create biphasic systems, the ability to effectively separate products from ionic liquid, and the reuse of ionic liquids are the advantages of ionic liquids as acidic catalysts demonstrated in this project..

Acknowledgments

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References

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