Science, Technology, Research
& Innovation for the Environment
STRIVE

SUMMARY OF FINDINGS
STRIVE Report No. 119

Safer Acid Catalysts

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In terms of the environment, green chemistry can bring significant reductions in environmental impacts from chemical processes. For industry, cost savings stemming from reduced chemical consumption and cheaper chemical manufacture are a stimulus for industry uptake of green chemistry methodologies. Green chemistry was prioritised under the EPA STRIVE research programme, where the development of safer, less toxic and biodegradable chemicals was highlighted as an important goal. This report details our progress towards this goal for a class of chemicals called acid catalysts.

Key Words: Green chemistry, toxicity, biodegradation, green chemistry metrics, cleaner synthesis, acid catalysis, asymmetric catalysis, organocatalysis, ionic liquids, imidazolium salts.

Background: European Union REACH (Registration, Evaluation, Authorisation, and Restriction of Chemical Substances) chemical control laws were implemented in 2007 to protect humans and the environment by ensuring information was available on the hazards of chemicals so they can be assessed and managed. This is now a global trend: for instance, amendments to TSCA (Toxic Substances Control Act) in the US in 2010 shifted the burden of demonstrating the safety of chemicals from the US Environmental Protection Agency to manufacturers. China's Ministry of Environmental Protection (formed in 2008) strengthened safety initiatives and recently greatly expanded the toxicity data requirement before import or production of chemicals not listed on their current chemical inventory. Current national policy includes the government's promotion and strategy of a SMART Green Economy, national priority areas (including processing technologies and materials), the EPA's 2020 Vision – Sustainable Use of Resources and EU policy Horizon 2020 and 2013 – COST Action CM1206 (Exchange of Ionic liquids), which demonstrate the relevance of green chemistry projects. Part of the research strategy was to replace 'traditional synthetic methods' with 'a greener alternative'.

The inherent advantage of green chemical transformations are improved resource efficiency. This is realised by: (i) reducing the quantity of chemicals required to produce the target material; (ii) reducing the number of steps to manufacture the product; and (iii) reducing the waste generated. In the first two points, one must consider the benefit of utilising less chemicals (including solvent), together with the positive effect on the environment (e.g. lower energy consumption, reduced CO_2 emissions, improved air quality, and less waste treatment) when producing these raw materials. Also, by reducing the toxicity and increasing the biodegradability of chemicals utilised, the waste stream can be more easily treated, avoiding the need for landfill or incineration. Green chemistry can thus lead to significant reductions on the impact on the environment. Cost savings due to reduced chemical consumption and cheaper chemical manufacture are a stimulus for industry uptake of green chemistry methodologies. The design of safer chemicals is a worthwhile goal. Anastas and Warner (1998) provided a roadmap for this when they published the 12 Principles of Green Chemistry. Fundamental to their approach was a combined interdisciplinary strategy where the toxicity and biodegradation assessment of chemicals (e.g. acid catalysts) is combined with a 'greener' or less environmentally damaging synthetic route for preparing them. Thus, the development of biodegradable imidazolium salts is a major and worthwhile goal. Our hypothesis was that the modifications performed to change the catalyst's molecular structure to improve performance would also improve biodegradation and reduce toxicity. This in turn results in reducing the negative impact on the environment.

Key points/ Findings

- The project successfully improved the activity of the acid catalysts, while maintaining excellent yields.
- The recommended final acid catalysts have low antimicrobial toxicity.
- In addition, green chemistry metrics to analyse the efficiency of the synthesis of the acid catalyst and waste generation were applied. By identifying the most environmentally damaging processes, and developing greener alternatives, we now have a cleaner synthesis of our recommended acid catalysts.
- A major challenge of the project was to prepare biodegradable acid catalysts. Predicting accurately biodegradation (i.e. computer modelling) of this class of compound (imidazolium salts) is not currently possible. This is in part due to the lack of experimental data to train modelling programmes. We successfully obtained biodegradation data for our imidazolium acid catalysts: however, none of these chemicals passed the CO_2 Headspace Test.
- The impact of the work over the duration of the project has been stepwise.
- The project's first publication reported catalyst performance only.
- The second combined performance and antimicrobial toxicity and was published in the leading Royal Society of Chemistry journal in the field, Green Chemistry in 2010.
- The latest dissemination is a series of three back-to-back papers in Green Chemistry, reporting catalyst performance, antimicrobial toxicity, biodegradation, green chemistry metrics and catalyst recycling. These papers are the triple front cover articles for the Green Chemistry 2013 October issue, with the first of the series also highlighted as a 'Hot Article' by reviewers.
- This justifies and validates the current research decision to our approach to jointly assess the toxicity, biodegradation, synthesis and performance of the catalysts at the development stage, which to the best of our knowledge, is unique to our Dublin City University (DCU)/Trinity College Dublin (TCD) team.
- When presenting our findings at conferences in Europe and the US, the overwhelming feedback is that this type of joint assessment should be the rule rather than the exception, and this is our key recommendation.

Recommendations

- Tandem catalyst performance and toxicity assessment has led to the development of a low antimicrobial toxicity and very active catalysts. This approach was successful and is advised for future studies;
- Boethlings' 'rules of thumb' for designing biodegradable molecules should be modified to account for poor biodegradation of catalysts studied;
- The use of green chemistry metric assessment successfully highlighted parameters which can be targeted for further improvements in the reduction of waste for catalyst preparation.

For Further Information

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This report is published as part of the EPA Science, Technology, Research and Innovation for the Environment (STRIVE) Programme 2007-2013. The full report is published by the EPA and is available from: http://www.epa.ie/pubs/reports/research/tech/strive119-saferacidcatalysts.html

Additional outputs from the project

Include three book chapters, two papers under review, project website, invitations to contribute to seminars (including a plenary talk at a major EU conference and environmental toxicology meetings in the US), organising an Irish Green Chemistry conference series at DCU, and the graduation of two PhD students.