

# New Heterogeneously Catalyzed Processes for Environmentally Benign and Sustainable Chemical Production

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## Introduction

Environmental concerns and regulations have been increasing in the public, political and economical world over the last 20 years, because quality of life is strongly connected to a clean environment. The impulse for developing new, more efficient and selective catalysts and for the realization of new and sustainable process technology is strongly related to environmental compatibility. Solid acid, solid base and solid acid-base, bifunctional catalysts play an important role in this [1]. More than 130 industrial processes are reported to be catalysed by such solids. For example, the use of solid acid catalysts instead of homogeneous Brønsted acids, such as  $\text{H}_2\text{SO}_4$ , and Lewis acids, such as  $\text{AlCl}_3$ , avoids the disadvantages of homogeneous catalysis, such as high salt formation, corrosion problems, waste disposal, water pollution and problems in sludge treatment. Furthermore, those heterogeneous catalysts can easily be separated from the reaction mixture and can be regenerated if necessary, i.e. recyclization and reusability will be given.

In addition, the application of renewable feedstocks contributes to a sustainable chemical production as well. The annual total consumption of organic raw materials in Germany is about 19 million tons; 75 % are based on crude oil and natural gas, 15 % on coal and 10 % on renewable feedstocks. These 10 %, however, correspond to 22 % of the value of all chemicals produced in the German chemical industry. Considering such figures for the use of renewables, one has to realize that there is a big margin between production costs and sale prices, resulting in a high profit. Therefore, and also due to the environmental constraints, there is a strong interest in Europe and in the USA to broaden the base for such feedstocks.

## Results and Discussion

Some examples of our work in this area will be presented:

- 1.) The selective conversion of mixtures of terpenes to the important intermediate p-cymene is of high commercial interest. Such terpenes are widely and cheaply available as by-products from the orange and lemon juice production as well as from pulp and paper industry. The valuable p-cymene can be used, e.g., in the fragrance industry (non-nitrated musks), as a biodegradable solvent and as intermediate for the production p-cresol.
- 2.) Metal-catalyzed oxidation of alcohols to carboxylic compounds is an important step for the synthesis of fine chemicals. Particularly, the oxidation of the primary hydroxyl group

in sugars and its derivatives such as starch and cellulose is important. The oxidized carbohydrates can be used as thickeners, as gelling agents, in paints, as resins, detergent co-builders, and as super absorbers (biodegradable diapers).

- 3.) By far the largest amount of lubricants and pressure media used worldwide is produced on the basis of mineral oil. In 1999, the consumption of lubricants in Germany was 1.159.900 t. In total, 520.000 t of lubricants were released into the environment. Therefore, the use of renewable feedstocks is of high interest. The aim of our work presented is to improve the stability of rapeseed oil against oxidation and hydrolysis by the addition of different carboxylic acids and alcohols to the double bonds in presence of environmentally friendly heterogeneous catalysts resulting in high yields.
- 4.) The production of biodiesel based on renewable feedstocks such as palm oil, rapeseed oil and soya bean oil is currently a very hot topic. During this process, about 10 mass% glycerol is produced as an inevitable side product. In 2015, an amount of about 1 mio t/a glycerol is expected. As a result of that, a lot of research is going on to convert this into high value added intermediates with a C3 building block. The conversion of glycerol to acrolein and acrylic acid in high yield, being competitive with the current technology based on propylene, was developed in our group in collaboration with Arkema France recently. That is part of a trend to get more fuels independent from crude oil.

More recent results will be added to these considerations.

## References

1. K. Tanabe and W.F. Hölderich, *Appl. Catal. A: General* **181**, 399 (1999).