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CATALYTIC CONVERSIONS OF BIOSOURCED RAW-MATERIALS: HETEROGENEOUS CATALYSIS

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1968 – 1972 Study of chemistry at the Technical University of Karlsruhe (TU),
1972 - 1975 Research on silylphosphanes under the supervision of Prof. Dr. G. Fritz, Institute for Inorganic Chemistry of the University of Karlsruhe, leading to doctorate
1976 – 1977 Postdoctoral research as a NATO-Scholar at M.I.T., Cambridge, Massachusetts, USA with Prof. Dr. D. Seyferth
1978 – 1992 Research Activities at BASF AG. In charge of several leading positions in research of heterogeneous catalysis. Member and representative of research in the 4 person steering committee of the BASF catalyst business profit center.

Since 01. April 1992
University professor and Director of the Department of Chemical Technology and Heterogeneous Catalysis at the University of Technology RWTH-Aachen ; TCHK = Technische Chemie und Heterogene Katalyse
Main research topics: heterogeneously catalysed synthesis of fine and intermediate chemicals such as caprolactam etc. as well as the use of renewable feeds as starting material. Acid / base catalysis, in particular zeolites as catalysts as well as oxidation catalysis are fields of interest.
More than 230 patents and approx , 300 papers on heterogeneous catalysis, co-editor of 4 books and Editor of 2 Special Issues on Industrial Catalysis for Applied Catalysis
Member of several editorial boards and international advisory boards. Several Awards, the most distinguished ones: The JSPS Fellowship for Research in Japan Spring 1997 and E.V. Murphree Award of the American Chemical Society for Industrial Chemistry and Chemical Engineering sponsored by ExxonMobil 2007 etc.

Abstract
The most pressing issues in our world today are global climate change, food production, dissipation of toxic materials, sustainable energy production and of course depletion of non-renewable sources. In the solution of these problems “green chemistry” and “green engineering” play a major role. Thus, we search for alternative reagents, alternative solvents, alternative products, alternative catalysts and alternative feedstock i.e. biosourced raw-materials. In particular the last two topics will be in the focus of this presentation.

Introduction
The annual total consumption of organic raw materials in Germany is about 19 million ton; about 90 % are based on crude oil and natural gas, 2 % on coal etc., as well as 8 % on renewable

feedstock. These 8 %, however, means 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 the production costs and the sale prices resulting in high profit. Therefore and also due to the environmental constrains there is a strong interest in Europe to broaden the base for such feedstock. Several examples will be discussed also in relation to chemical engineering aspects and its scale up procedures.

Results and discussion

Conversion of mixtures of terpenes to p-cymene / p-cresol

The selective conversion of mixtures of terpenes to the important intermediate p-cymene is of a 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 biodegradeable solvent and as intermediate for the production p-cresol as a precursor for the most important antioxidant di-tert.-butyl-p-cresol. The investigation of the catalytic behaviour over various Pd-modified silica catalysts results in yields of up to 98 % depending on the mixture of the starting material

Flavours and aroms based on limonene and pinene

In addition to this topic a flavor for the production of fragrances and aroms based on renewables will be touched, too. Among them the synthesis of the sandalwood fragrances, the grapefruit arom and the mangofruit arom will be discussed.

Biodiesel of first generation from triglycerides in presence of a bifunctional catalyst

The production of ´biodiesel based on renewable feedstock such as palm oil, rapeseed oil and soya been oil is a very hot topic of our days. This topic will be discussed using new acid–basic bifunctional catalysts based on Lanthanoid oxides supported on various carriers under different reaction conditions. Thereby, we can manage a simultaneous esterification and transesterification of trigylcerids which contain even a high amount of free fatty acids. That means there is no purification of the triglycerides or their preesterification necessary anymore and very cheap oil and fats such as brown grease from pork can be applied. Yields of FAME biodiesel up to 98 % can be achieved. In addition high grade glycerol with 98 % is obtained.

Glycerol conversion to acrolein and acrylic acid

In the Biodiesel production, glycerol is produced as inevitable side in 10%. 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 that in high value added intermediates with a 3 C building block. The conversion of glycerol to acrolein and acrylic acid in high yields being competitive to the current technology based on propylene was developed in our group recently. That is a trend to get more independ from crude oil based petrochemicals.

New lubricants based on chemically modified oleochemicals

By far the largest amount of lubricants and pressure media used world wide is produced on the basis of mineral oil. In 1999, the consumption of lubricants in Germany was 1.159,900 t. 10 % of that amount was employed for loss lubrication (e.g. for chain saws or as release agents). In total, 520.000 t of lubricants are released into the environment. Therefore the use of renewable feedstock 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 the presence of environmentally friendly heterogeneous catalysts resulting in high yields.

Production of carboxylic acids based on sugars and starch

Metal-catalyzed oxidation of alcohols to carboxylic compounds is an important step for 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 thickening, as gelling agents, in paints, as resins detergents co-builders, and as super absorbers (biodegradeable diapers). Only a few reports describe procedures for the oxidation of primary hydroxyl groups that leave the secondary hydroxyl groups still intact. Such a regioselective oxidation can be mediated by 2,2,6,6,-tetramethylpiperidinyl-1-oxy (TEMPO), but unfortunately thereby an environmentally hazardous hypochlorite/bromide system is used. Therefore our

investigations focus on heterogeneously Ag-catalyzed procedure. For example, 99 mol % selectivity to methyl-α-D-glucopyrasiduronic acid was obtained at 90 % conversion of the pyranoside over a silver-celite catalyst.

Conclusions

• At present, in most cases products obtained from renewable raw materials are not competitive with products based of petrochemistry. That will change rapidly when the oil price still rises and oil resources will diminish. There are only a few commercialised examples right now.

• In the commercialization of new technology based on biosourced raw-materials there is a fight against paid off plants based on petrochemistry

• There is no doubt: The trend is to use the synthesis performance of the nature due to the fact of the future lack of fossil energy sources. Production processes based on renewables need less energy and raw materials as well as create less waste and by-products.

• Extensive use of the carbon framework of renewable resources for the synthesis of chemicals, i.e. starting from a higher level.

• In the long run, renewable resources are considered to become a viable solution. Their catalytic processing will make it possible to replace the fossil feedstock oil and coal.

• Chemists, biotechnologists and growers are requested to work together interdisciplinary to develop e.g. mutated oils and fats as renewable feedstock for the chemical industry / oleo chemistry.

References

See the presentation