Solid acid catalysed conversions of oleochemicals
Koster, R.

Citation for published version (APA):
CHAPTER 1

Introduction

Oleochemistry

Oleochemicals are chemicals made from (vegetable or animal) oils and fats. Oils and fats are tri-esters of fatty acids and glycerol, so-called triglycerides. The difference between fats and oils is that at ambient temperatures fats are solid and oils are liquid.

Oleochemicals are an environmentally attractive source of chemicals, compared with chemical derived from petroleum, as they are basically renewable feedstocks and essentially CO₂ neutral. Examples of oleochemical products are fatty acids, glycerol, fatty alcohols, fatty amines, and metallic soaps. Oleochemicals are used in a wide range of applications such as in lubricants, soaps and detergents, cosmetics, pharmaceuticals, food additives, paints and coatings, and printing inks [1].

The raw materials for oleochemicals can grow in many parts of the world. A large part of the vegetable oils such as coconut, palm and palm kernel oil is coming from tropical countries. In more temperate climates production of soybean, rape and sunflower oils is possible. Wood or tall oil (by-product form the paper pulp industry) is another source of vegetable oils [1].

For the year 2001, world production of oils and fats is estimated at 117 million tonnes with soybean oil as number one at about 25 million tonnes and palm oil as number two at 23 million tonnes [2]. Approximately 14 % is used for the production of oleochemicals [3]. World production of oils and fats has been increasing steadily at 3.35% per annum for the period from 1990 - 2000.
Natural oils and fats are not based on a single fatty acid. Each oil type contains a mixture of fatty acids in proportions that depend on the source of the oil. In most oils they occur in the form of triglycerides. These are esters in which one molecule of glycerol is chemically combined with three molecules of fatty acid. Natural fatty acids have all straight chains of carbon atoms with a terminal carboxyl group. Predominantly these acids have an even number of carbon atoms and an essential difference between any two adjacent members of the series is the length of the carbon atom chain and the degree of unsaturation. The most abundant fatty acids are those with 16 and 18 carbon atoms.

Figure 1.1: Basic oleochemical reactions

The basic step for transforming animal and vegetable oils and fats into oleochemicals is hydrolysis, the splitting of triglycerides into glycerine and fatty acids (Figure 1.1). The triglycerides can also be directly transformed into methyl esters with excess methanol using an alkaline catalyst.

Distillation is used to purify the crude fatty acids under vacuum. Separation of fatty acids yields a liquid fraction (unsaturated acids, mainly oleic acids) and a solid fraction (saturated acids, mainly stearic acids). Fractional distillation is used to separate a mixture of fatty acids according to chain length.
Fatty acids can be converted into a number of oleochemical products, including dimers of unsaturated fatty acids, fatty esters, fatty amides, fatty nitriles and its derivatives, and metallic soaps.

**Dimerisation of unsaturated fatty acids**

Dimerisation of unsaturated fatty acids is an important process in the oleochemical industry. Three major products are made in this liquid phase batch process: isostearic acid, dimers and trimers. The three products each consist of numerous different compounds caused by the use of natural feeds, consisting of a variety of fatty acids, and the occurrence of several side reactions: cis/trans isomerisation, double bond shift, branching, ring formation, aromatisation, hydrogen transfer and lactone formation. [4, 5]

Dimers and trimers are mainly used as components in polyamides, e.g. in hot melt adhesives, epoxy-coatings and flexographic printing inks. The monomer fraction of the product is applied in lubricants or cosmetics [1].

A simplified reaction scheme is shown in Figure 1.1.

![Reaction scheme](image)

*Figure 1.2: Dimerisation reaction scheme*

In 1918 the first patent on polymerisation of unsaturated fatty acids appeared [6]. The patent revealed the thermal polymerisation of polyunsaturated fatty acids. An important disadvantage of the thermal polymerisation is the poor quality of the product: high trimer content and dark colour. In 1954 Emery Industries replaced the thermal process by the
montmorillonite clay-catalysed dimerisation, which improved product quality significantly
[7].

Montmorillonite clay is nowadays still applied as catalyst, since it is by far the most active heterogeneous catalyst found in scientific and patent literature. The structure and properties of these clays are therefore discussed in the next paragraph.

**Montmorillonite Clay**

Clays are layered structures and in the case of montmorillonite clays each layer consists of an octahedral sheet between adjacent tetrahedral sheets. This structure of the layer is typical for the 2:1 pyrophillite class of clay minerals and is depicted in Figure 1.3. The 2:1 phyllosilicates are divided into di- and trioctahedral phyllosilicates. In dioctahedral 2:1 phyllosilicates, \( \text{Al}^{3+} \)-cations occupy two out of three octahedral positions. In trioctahedral phyllosilicates all octahedral positions are occupied by divalent metal cations. Montmorillonite is a dioctahedral phyllosilicate like pyrophillite, but contains isomorphous substitution sites. \( \text{Mg}^{2+} \) substitutes \( \text{Al}^{3+} \) (~1 out of 4 \( \text{Al}^{3+} \)) in the octahedral sheet and \( \text{Al}^{3+} \) substitutes \( \text{Si}^{4+} \) (~1 out of 25 \( \text{Si}^{4+} \)) in the tetrahedral sheet [8, 9].

**Figure 1.3:** **Structure of a dioctahedral 2:1 phyllosilicate**

The extent of substitution in the sheets is different for each (natural) clay, but in montmorillonite substitution in the octahedral position is most abundant. Iron is another element in the montmorillonite structure occupying a small part of the octahedral positions.
Substitution leads to an excess negative charge of the layers, which is neutralised by
interlayer metal cations and protons. The interlayer metal cations are acidic by polarisation of
their hydration shell. Protons and metal cations in the interlamellar space balance the negative
charge of the layers, originating from octahedral and tetrahedral isomorphous substitution.
Interlayer metal cations are easily hydrated and can, therefore, cause the clay to swell [10].
Swelling may proceed up to the point where four or more layers of water are accommodated
in the interlayer, depending on the type of interlayer cation, relative humidity, and the charge
of the sheets [11, 12].

**Esterification**

Esters and water are formed in a condensation reaction of an alcohol and an acid.
Alternatively, esters can be formed in a reaction of an alkene with an acid or in a
transesterification (alcoholysis, acidolysis) reaction in which the alcohol or acid part of the
ester is exchanged.

Esters are used in the production of many everyday products, as fragrances,
lubricants, flavors and detergents. Esterification is also a key step in the oleochemical
industry; the fatty acid esters are used in foods, textiles and cosmetic applications [1].

Industrially, esterification reactions are mostly carried out in batch processes using
homogeneous catalysts. Typical catalysts are (Brønsted acidic) sulfuric acid or (Lewis acidic)
Sn-octoate. Brønsted acidic homogeneous catalysts are corrosive and need to be neutralised
after reaction (forming salts) and Lewis acidic, metal containing, catalysts need to be
removed carefully after reaction. The use of heterogeneous catalysts in esterification is
preferable, since these are easily separated from reactants and products and can be re-used.

Although solid acids are already used in several industrial processes, their use in
oleochemicals production is still limited. Apparently, implementation of a solid acid in liquid
phase esterification is not straightforward. This can be explained by realising that most solid acids are rather hydrophilic, which may lead to inhibition of the active sites by the water that is formed in the esterification reaction [13].

Scope

The catalysis of two important reactions in oleochemistry, esterification and dimerisation, is studied. The aim of this work is to increase our knowledge on active sites of the investigated heterogeneous catalysts and on the reaction mechanisms at the catalytic surface. This should eventually lead to a more rational design and optimisation of heterogeneous catalysts for these reactions, allow for the replacement of homogeneous acidic catalysts and lead to a higher selectivity in the conversion and synthesis of these oleochemicals, resulting in a reduction of waste streams and by-products.

References

2. Oils and Fats World Congress 2002 (OFIC), congress website
6. J. Craven, Br. Pat. 121.777 (1918)


