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Paper B(Ch)

Chemistry

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Patent application

Process for the hydrogenation of oils

[001] The invention is directed to a process for the hydrogenation of oils such as fish oil or soybean oil, to increase the melting point of the oils. Hydrogenated oils are useful in cooking, as lubricants and in food products.

[002] The oils are not completely hydrogenated to the highest possible melting point (i.e. to a solid fat), but to a value intermediate between the said highest possible melting point and the melting point of the original oil. The oil is hydrogenated catalytically in the presence of hydrogen. Hydrogenation catalysts, such as nickel or precious metal catalysts are used.

[003] The desired melting point is -10 to 15 °C.

[004] In natural oils, such as fish oil, soybean oil or sunflower oil the cis-isomer predominates. Hydrogenation processes not only increase the melting point, but also cause isomerisation and thus result in the formation of trans-isomers from cis-isomers. In the conventional catalytic hydrogenation of soybean oil or fish oil a product is obtained having a melting point -10 to 15 °C. The original trans-isomer content of the oil of about 15 % is increased to about 55 % (according to DIN 38279/2000-1).

[005] The consumption of trans-isomers is associated with health hazards therefore the content of trans-isomers in the hydrogenated edible oils should be kept as low as possible.

[006] Typical reaction conditions for hydrogenating edible oils comprise the use of nickel hydrogenation catalyst, a temperature of 175 to 200 °C and 0.7 to 2 bar hydrogen pressure.

[007] It would be very desirable to have a catalytic hydrogenation process for edible oils, which produces hydrogenated edible oils with the required melting point and having reduced amounts of trans-isomers as compared to conventional hydrogenation processes.

[008] The present invention provides a process for the hydrogenation of edible oils in the presence of a precious metal catalyst and hydrogen. A precious metal catalyst is used, comprising a solid support and precious metal particles, preferably precious metal nanoparticles, on the support.

[009] Preferably, the precious metal is present in the form of nanoparticles having an average particle size of 1 to 12 nm, according to ASTM 99999/2000.

[010] According to a preferred embodiment the catalyst consists of a combination of three components. In this preferred embodiment the catalyst, in addition to the support and the nanoparticles, further comprises a polymer containing a heterocyclic group. The heteroatom is preferably nitrogen. This catalyst has the further advantage that the process not only produces a lower concentration of trans-isomers, but is also more active in the hydrogenation of oils. A more active catalyst means that the amount of time needed to obtain the desired melting point is shorter.

[011] The catalyst is produced using a conventional method. In case a polymer is present in the catalyst, the polymer is preferably dissolved in the solution of a precious metal precursor. Such catalysts are known and they are used to remove nitrous oxide from flue gases.

[012] Generally the concentration of precious metal is 0.01 to 15 wt.% calculated on the weight of the catalyst in reduced form, preferably 0.1 to 5.0 wt.%.

[013] The precious metal may be selected from the group consisting of platinum (Pt), palladium (Pd), iridium (Ir), rhodium (Rh), ruthenium (Ru), gold (Au), silver (Ag) and combinations thereof. The most preferred metal is platinum.

[014] The support material may be any material that remains stable during the process. This requirement is for example met by carbon, silica or alumina. It is also possible to use molecular sieves. The support is preferably porous with pores having an average pore size of 0.05 to 2 μm.

[015] The polymers containing a heterocyclic group, preferably comprise the heterocycle as a side group. The heterocyclic group forms a complex with the metal atoms in the particles during the hydrogenation. The most preferred polymer is PVP (polyvinylpyrrolidone) as this polymer is believed to provide the best results.

[016] The concentration of polymer in the final catalyst may vary widely. A concentration of up to 15 wt.% or even more calculated on the weight of the catalyst in reduced form is suitable. If less than 0.1 wt.% polymer is used, however, no effect is observed.

[017] The hydrogenation of the oils, preferably fish oil, can be done in a manner th usual in the art. Temperature, duration and hydrogen pressure can be suitably selecte to take into account the desired melting point and concentration of trans-isomers in the product. In general the temperature will be 30 to 200 °C, the hydrogen pressure 1 to 200 bar (absolute) and the duration will be 5 min to 4 hours.

[018] The following examples illustrate the invention:

<u>Example 1: Hydrogenation of fish oil to produce a product with a melting point of 0 to 10 °C</u>

[019] 50 g of fish oil was hydrogenated at a hydrogen pressure of 5 bar and a temperature of 50 °C with a platinum silica-supported catalyst, containing 1 wt.% of platinum nanoparticles, having an average particle size of 4 nm, and 0.1 wt.% of PVP. The original oil had a melting point of -44 °C and contained 15 % of trans-isomers. The hydrogenation was carried out until the melting point was 5 °C. This took 35 minutes. The oil obtained contained 29 % of trans-isomers.

Examples 2 - 8

[020] The experiment of Example 1 was repeated, using different concentrations of PVP. In examples 6 to 8 the melting point of the product was set to be 10 °C. The results are given in table 1, below.

Table 1

Example	Melting point (°C)	PVP concentration (wt.%)	Time (min)	Average particle size (nm)	Platinum concentration (wt.%)	Trans isomers (%)
2	5	0	40	4	1	40
3	5	0.05	40	4	1	40
4	5	0.3	15	4	1	23
5	5	1.5	20	4	1	20
6	10	0	50	4	1	45
7	10	1.5	28	4	1	31
8	10	1.5	35	4	1	29

Claims

1. Process for the hydrogenation of edible oils in the presence of hydrogen and of a precious metal catalyst, the catalyst comprising a solid support and precious metal particles, preferably precious metal nanoparticles, on the support.

2. Process according to claim 1, wherein the support is porous, the pores having an average pore size of 0.05 to 2 µm.

3. Process according to claim 1 or 2, wherein the catalyst further comprises a polymer, containing a heterocyclic group having at least one heteroatom, preferably nitrogen.

4. Process according to claims 1 to 3, wherein the precious metal nanoparticles have an average particle size of 1 to 12 nm.

5. Process according to claims 1 to 4, wherein the edible oil is fish oil.

6. Process according to claims 1 to 4, wherein the edible oil is soybean oil.

Communication under Article 94(3) EPC

1. The examination is based on the application documents as originally filed.

2. Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure:

   D1: Handbook of Fish Oil Hydrogenation, 1965

   D2: EP-A-3 000 001, published on 03.01.2007

3. Claim 2 violates Article 84 EPC as the average pore size is not clearly defined. As is well-known, there are various standard methods for determining pore sizes, which give different results. The application does not disclose a method for determining the average pore size.

4. Claims 1 and 3 to 5 are not novel (Article 54(2) EPC). D1 discloses the hydrogenation of fish oil using a supported precious metal catalyst. Claims 1,3 and 5 are not novel over D1. D2 discloses the same process as the present application. As all the features of claims 1,4 and 5 are disclosed in D2, these claims lack novelty.

5. Claim 6 is obvious over D1 and D2 (Article 56 EPC). Although D1 and D2 do not disclose the use of soybean oil, it is well known that soybean oil is an oil used in food products, as is fish oil. As the applicant himself considers fish oil and soybean oil to be equivalent (see also paragraph [004]) the use of soybean oil would be obvious.

6. If the applicant wishes to maintain the application, new claims should be filed to take the above objections into account. Care should be taken to ensure that the new claims comply with the requirements of the EPC in respect of clarity, novelty, inventive step and if necessary unity (Articles 84, 54, 56 and 82 EPC). Care should further be taken that any amendments do not introduce subject-matter which extends beyond the content of the application as originally filed (Article 123(2) EPC).

7. In the letter of reply, the problem-solution approach should be followed, in particular the difference between the new claims and the prior art disclosed in the documents D1 and D2 should be indicated. The technical problem underlying the invention in view of the closest prior art and the solution to this problem should be readily derivable from the statement of the applicant.

8. In order to facilitate the examination as to whether the new claims contain subject-matter which extends beyond the content of the application as originally filed, the applicant is requested to indicate precisely where in the application documents any amendments proposed find a basis (Article 123(2) EPC and Rule 137(4) EPC).

<u>Document D1</u>

Handbook of Fish Oil Hydrogenation, 1965

[001] A method for hydrogenating fish oil to a product with an increased melting point and a low trans-isomer content has already been investigated extensively. One method for the hydrogenation of fish oil uses hydrogenation conditions, which promote hydrogenation in relation to isomerisation. This method uses a low temperature of 30 40 °C and a high hydrogen pressure of 150-200 bar (absolute). Using this method it is possible to obtain a trans-isomer content of about 20% (according to DIN 38279/2000-1) for a hydrogenated oil with a melting point of 5 °C. This reaction typically takes from 3 to 4 hours.

[002] The catalytically active material is in metallic form and is usually nickel or a precious metal, present on a porous solid support (usually silica). The catalyst is in suspension in the fish oil.

[003] In this reaction the catalyst has to be filtered from the oil after the reaction has completed. The effect of adding various materials to the catalyst on its filterability has been investigated. Molecular sieves and polymers (polyvinylpyrrolidone, polyethylene and polyvinylchloride) were tested in a concentration of 0.05 wt.% calculated on the weight of the reduced catalyst. Polyvinylpyrrolidone is a polymer containing a heterocycle as a side group. The heteroatom is nitrogen. It was found that these additives did not improve the filterability, nor did they influence the reaction in any way.

Document D2

EP-A-3 000 001

[001] The present invention is concerned with the hydrogenation of oils, in particular fish oil. Vegetable oils such as sunflower oil can also be treated by the process.

[002] This hydrogenation is necessary, among other reasons, to increase the oxidation stability and to obtain an oil with the desired melting point. Hydrogenation can take place utilising conventional hydrogenation catalysts, such as nickel or precious metal catalysts.

[003] The present invention improves the yield of the hydrogenation by the use of a supported platinum nanoparticle catalyst. The support is porous silica. The metal particles have an average particle size of 2 to 8 nm, according to ASTM 99999/2000. The concentration of platinum in the catalyst is in the conventional range of 0.01 to 2.5 wt. %.

[004] It has surprisingly been found that with this catalyst it is possible to hydrogenate fish oil to a desired melting point in a high yield and in a short time.

Claims

1. Process for the hydrogenation of edible oils in the presence of a precious metal catalyst and hydrogen, the catalyst comprising a solid support and platinum nanoparticles on the support.

2. Process according to claim 1, wherein the amount of platinum is 0.01 to 2.5 wt.%, preferably 0.5 to 1 wt.%, of the catalyst.

3. Process according to claim 1 or 2, wherein the edible oil is fish oil.

Letter from the applicant

Smelly Fats Ltd.,
Oil Alley,
Whale City, Ireland

Fish & Co.,
Patent Attorneys,
Cod Avenue 15,
Fishmarket, Ireland

Dear Mr Fish,

As you know, my firm is especially active in the hydrogenation of fish oils to produce oils having an increased melting point. It is very important that my patent application will cover this aspect of the invention.

I have carefully looked at the objections of the Examiner and I do not think that they are a hurdle that cannot be overcome.

The average pore size of the support material was, of course, determined by nitrogen adsorption, using our internal standard method for calculation. I think this is clear.

Please find enclosed with this letter a set of claims that I have drafted to overcome the other objections of the Examiner. As you can see I suggest restricting the precious metal particles to nanoparticles. The term 'nanoparticles' has become a well defined term in the field of catalysis and refers to particles with an average particle size of 1-100 nm. Catalysts with larger particles give worse results.

The process is also inventive over the Handbook D1 and the patent application D2 combination of precious metal nanoparticles and a polymer on a support is not suggested by these two documents.

Please make sure that you file the response today. In case you think that my set of claims has to be amended to get a patent granted immediately, you may do so, but make sure that the important aspect is still covered. Starting today, I will be away on a fishing trip, which means that I am not available for answering further questions.

Yours sincerely

Marcus Herring

Claims proposal

1. Process for the hydrogenation of edible oils in the presence of hydrogen and of a precious metal catalyst, the catalyst comprising a solid support, ~~and precious metal particles, preferably~~ precious metal nanoparticles on the support and a polymer.

2. Process according to claim 1, wherein the support is porous, the pores having an average pore size of 0.05 to 2 μm, as measured by nitrogen adsorption.

3. Process according to claim 1 or 2 wherein the ~~catalyst further comprises a~~ polymer containi~~ng~~s a heterocyclic group having at least one heteroatom, preferably nitrogen.

4. Process according to claims 1 to 3, wherein the precious metal nanoparticles have an average particle size of 1 to 12 nm.

5. Process according to claims 1 to 4, wherein the edible oil is fish oil.

6. Process according to claims 1 to 4, wherein the edible oil is soybean oil.