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Production of hydrogenated methyl esters of palm kernel and sunflower oils by employing rhodium and ruthenium catalytic complexes of hydrolysis stable monodentate sulfonated triphenylphosphite ligands

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ABSTRACT

This study deals with the hydrogenation of renewable polyunsaturated methyl esters of palm kernel and sunflower oils to the saturated (C18:0) methyl stearate (MS) catalyzed by rhodium and ruthenium complexes modified with hydrolysis stable monodentate sulfonated triphenylphosphite (STPP) ligands under mild reaction conditions in the absence or presence of organic solvents. Superior selectivities up to 95.8 mol% of MS were achieved by Rh/STPP catalysts compared with the much lower selectivities (28.0–43.2 mol%) of MS obtained by rhodium catalysts modified with conventional triphenylphosphite or triphenylphosphine ligands. The bulkiness of transition metal STPP catalytic system which is in the form of a triisooctylammonium salt offers the possibility of the easy separation of the catalyst from the reaction mixture by means of a membrane. The hydrogenation reaction of the polyunsaturated C18 esters part of palm kernel oil and sunflower oil methyl esters toward the desired saturated product MS is an interesting catalytic reaction because it could acts as a model reaction for studying the hydrogenation of edible vegetable oil triglycerides to hardfats. Hardfats can be further subjected to interesterification reactions with liquid edible vegetable oils to yield foodstuffs with zero amounts of *trans*-fats. Very recent investigations have questioned whether there really are direct associations between hardfat consumption and a higher cardiovascular disease risk. Furthermore, MS could be used as a starting material of selective heterogeneous catalytic hydrogenolysis reaction of the C18:0 fatty ester to the corresponding saturated C18:0 stearyl alcohol which is an important industrial fatty alcohol.

1. Introduction

Vegetable oils and their derivatives are important feedstocks for the industry with a broad spectrum of applications such as in foodstuff chemistry, pharmacy, cosmetics, plastics, detergents, biolubricants and in the energy field with the production of 1st generation biodiesel fuel mainly by transesterification reactions with methanol to obtain fatty acid methyl esters (FAME's) [1–9]. Catalytic hydrogenation of renewable vegetable oils and their derivatives constitutes a major unit process in the chemical industry. In hydrogenation processes of C═C units in unsaturated fatty acids of vegetable oils heterogeneous catalytic systems based on nickel, palladium, copper, copper-chromite, platinum, etc. are commonly used [1,2,5,7–9]. Heterogeneous nickel-based-catalyst was the choice of the edible oils hydrogenation industry which has a long history, started in 1902 with the first patent filed by Wilhelm Normann [10,11] for the liquid phase catalytic hydrogenation process of unsaturated fatty oils, in 1906 the British firm Joseph Crosfield & Sons developed the industrial hydrogenation process using as feedstock whale oil, and in 1911 the first commercial plant of Procter & Gamble went on stream with the appearance of the first industrially produced shortening, named "Crisco", obtained by hydrogenation reactions using cottonseed oil feedstocks [12–15]. In the past, the so-called hardening processes of edible oil partial hydrogenation were carried out over commercial Ni-based heterogeneous catalysts in industrial scale which produced up to 45% *trans*-fats [15]. The aims of traditional hardening of edible oils were to increase their melting temperature and thus increasing the consistency for use as margarine and improving the oxidative stability while an important amount of the C═C units in the fatty acid chain

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was *cis*/*trans*-isomerized. In recent years the negative health effects of *trans*-fats received increasing attention because they were considered to be strongly correlated with a higher concentration of plasma LDL-cholesterol and consumption of *trans*-fats provides no apparent nutritional benefit and possesses a considerable potential for harm [16–23]. Regulations were introduced first in Denmark by January 2004 to restrict the use of industrially produced *trans*-fats in edible fats to 2 wt% in any food product making possible that people consume <1 g industrially produced *trans*-fats per day and decisions have been made in USA in January 2006 to declare the *trans*-isomers contained in fatty foodstuffs which resulted in a demand for products with lower *trans*-isomers content [16–23]. Therefore, there is increasing interest in the development of new industrial partial hydrogenation processes of edible oils producing low amounts or preferably zero amounts of *trans*-fats. There are several other methods to reduce *trans*-fats in foodstuffs such as blending, fractionation, interesterification and the most versatile way for producing zero *trans*-fats is the full hydrogenation of vegetable oils to saturated hardfats combined with interesterification reactions of liquid edible oils [19,20,22,24–38]. Interesterification reactions between fully hydrogenated fat and liquid vegetable oil involve changes in the distribution of the fatty acid moieties among the glycerides of the precursors compared to their original composition resulting in a change of the properties in the mixture [38]. Current cardiovascular guidelines encourage low consumption of saturated hardfats based on results of studies in the 1950s which showed that there is a direct association between consumption of saturated fats and cardiovascular disease (CVD). However, a very recent investigation [39] based on 76 studies with 659 300 participants (27 of these studies are randomized controlled trials possessing a higher strength of evidence with 103 000 participants) has not clearly provided supportive evidence for current cardiovascular guidelines that encourage low consumption of saturated hardfats. Further studies [40–42] have also questioned whether there really are associations between saturated hardfat consumption and higher CVD risks. Therefore, nutritional guidelines on saturated hardfats and cardiovascular guidelines as well, may require a reappraisal to reflect the results of current investigations.

It was demonstrated that one of us together with Fell and Bahrmann [43–46] developed a novel class of ligands namely monodentate and polydentate sulfonated phosphites which are hydrolysis stable systems and successfully applied in the rhodium catalyzed hydroformylation of olefins to produce aldehydes with higher selectivities toward the desired linear aldehydes, i.e. higher *n*/*iso*-aldehydes ratio of 80/20, with even higher rates compared to their corresponding rhodium catalysts modified with conventional triphenylphosphite (*n*/*iso* ratio = 66/34) or triphenylphosphine (*n*/*iso* ratio = 67/33) ligands under mild reaction conditions in organic solvents. Favre et al. [47] used such sulfonated phosphite ligands to modify rhodium catalysts for the hydroformylation of olefins in ionic liquids and could easily separate the organic phase containing the products from the ionic liquid phase containing the catalyst by a simple phase separation. Recycling experiments proved that the high *n*/*iso*-ratios of the aldehydes obtained with Rh/sulfonated phosphites, which were also higher compared to their corresponding rhodium catalysts modified with phosphines, remained high in two consecutive runs.

We report here the development of the hydrogenation of C=C units of renewable methyl esters of palm kernel and sunflower oils catalyzed by rhodium and ruthenium complexes modified with hydrolysis stable sulfonated triphenylphosphite (STPP) monodentate ligands in organic solvents [48]. The renewable FAME's of palm kernel and sunflower oils act as model raw materials for studying the full hydrogenation of their corresponding vegetable oils to hardfats which are to be further subjected to interesterification reactions with liquid vegetable oils to yield foodstuffs with zero amounts of *trans*-fats. The bulkiness of the transition metal STPP catalytic system [48] which is in the form of a triisooctylammonium salt could offer the possibility of the easy separation of the catalyst from the reaction mixture by means of a membrane [63] which could be made from materials such as crosslinked polyolefins, poly(vinylidene fluoride), polyamides, etc. and this membrane catalyst separation technique has to be developed.

2. Experimental

2.1. Materials

Hydrogen (quality 5.0) was purchased from Air Liquide Hellas A.E.B.A. (Athens) and was used without further purification. $RhCl_3 \cdot 3H_2O$ and $RuCl_3 \cdot 3H_2O$ were purchased from Acros Organics and Alfa Aesar, respectively, and both used as received. Methanol and toluene were purchased from SDS, diethyl ether from Sigma–Aldrich and methyl acetate from Merck–Schuchardt. All organic solvents before use were dried through activated molecular sieves 4 Å which were purchased from SDS and used after filtration over 0.2 μm filter unit (Millex-FG of Millipore). The 65 wt.% aqueous solution of 4-hydroxybenzenesulfonic acid, triisooctylamine and triphenylphosphite were purchased from Sigma–Aldrich. Triphenylphosphine was purchased from Fluka. Demineralized water was deoxygenated in an ultrasound bath under vacuum for 2 h. During the deoxygenation, the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon. To remove oxygen the procedure was repeated three times. The renewable starting materials methyl esters of palm kernel oil (Edenor® ME PK 12-18 F) and methyl esters of sunflower oil (Sunflower Fatty Acid ME®) were supplied by Cognis GmbH and used without any further purification.

2.2. Preparation of the sulfonated triphenylphosphite triisooctylammonium salt (STPP)

A 2000-ml five-necked, round-bottom flask, equipped with a mechanical stirrer, a thermometer, a dropping funnel and a condenser, which was previously evacuated, heated by a heat gun and filled at room temperature with argon, was charged with 160.5 g of a 65 wt.% aqueous solution of 4-hydroxybenzenesulfonic acid [104.3 g (0.6 mol) 4-hydroxybenzenesulfonic acid] and 150 ml of deoxygenated demineralized water. A mixture of 212.2 g (0.6 mol) triisooctylamine (TiOA) in 500 ml of dried toluene was added dropwise through the dropping funnel and stirred intensively for a period of 3 h at room temperature. After phase separation the colorless aqueous phase was discarded and the orange colored 4-hydroxybenzenesulfonic triisooctylammonium/toluene organic upper phase was dried over activated Na_2SO_4 for overnight. After separation of Na_2SO_4 by filtration, the 4-hydroxybenzenesulfonic triisooctylammonium/toluene organic phase, was heated under reflux in a Dean–Stark apparatus for 12 h to remove last amounts of water from the organic mixture.

A solution of 62.5 g (0.2 mol) triphenylphophite and 5 g (0.01 mol) TiOA in 150 ml dried toluene was added dropwise to the 4-hydroxybenzenesulfonic triisooctylammonium/toluene mixture under stirring at 140 °C for 1 h. The condenser was than replaced by a distillation unit. Toluene was removed by distillation at 110 °C at first. The distillation of phenol, which is the byproduct of the transesterification reaction, was followed at 80–85 °C under 17 Torr vacuum within a period of 12 h and more phenol was distilled at 35 °C under 1 Torr for 6 h to give a total amount of 40.6 g of removed phenol. The yield of the transesterification reaction, based on the total amount of removed phenol by distillation,