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Novel Full Hydrogenation Reaction of Methyl Esters of Palm Kernel and Sunflower Oils Into Methyl Stearate Catalyzed by Rhodium, Ruthenium and Nickel Complexes of Bidentate Hexasulfonated *o*-Phenylendiphosphite Ligands

Niki Kaika[1] · Christina Panopoulou[1] · Eleni Anagnostopoulou[1] · Christos Fakas[1] · Panagiotis Lilas[1] · Dimitra Stavroulaki[1] · Georgios Papadogianakis[1]

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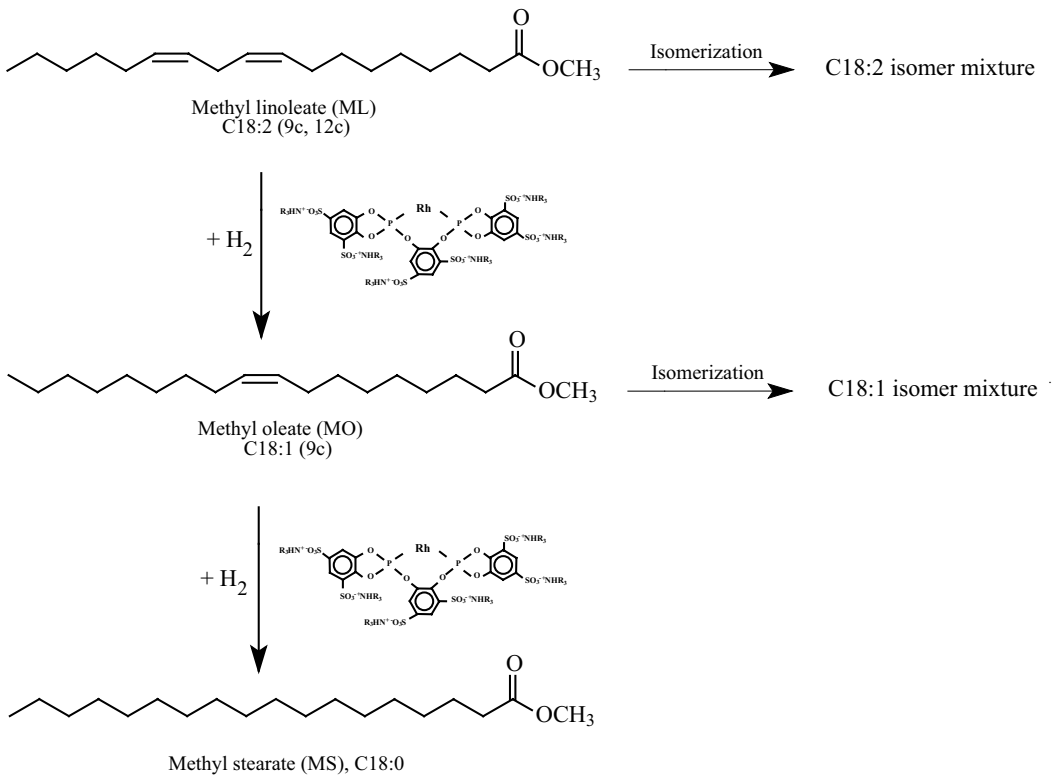
Abstract

High catalytic activities (TOF = 8680 h^{-1}) have been achieved by novel rhodium catalysts modified with the chelating sulfonated phosphite ligand hexasulfonated *o*-phenylendiphosphite in the hydrogenation reaction of renewable methyl esters of sunflower oil under mild reaction conditions and a low rhodium concentration of 50 ppm in methanol.

Graphical Abstract



Extended author information available on the last page of the article

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Keywords Hydrogenation · Methyl esters of palm kernel and sunflower oil · Rhodium, ruthenium and nickel · Bidentate sulfonated phosphite · Zero *trans*-fats

1 Introduction

Nowadays, renewable vegetable and tropical oils with their derivatives play an important role in the development of Green/Sustainable Chemistry because they are feedstocks for biorefineries with a broad spectrum of applications such as in foodstuff chemistry, detergents, cosmetics, pharmacy, plastics, biolubricants and in the energy production with the manufacture of biofuels with excellent fuel properties thus contributing to an effective management of greenhouse gas emissions and because of the depleting trend of conventional fossil feedstocks [1–10]. Vegetable oils are used for the production of 1st generation biodiesel fuel by transesterification reactions with methanol to fatty acid methyl esters (FAMEs) and in hydrotreating reactions in conventional oilrefineries to produce bio gas oil which is a mixture of mainly C_{11}–C_{18} linear and branched paraffins with a typical gas oil boiling range and belongs to the 2nd generation biodiesel fuel [1–10]. Full hydrogenation reactions of renewable polyunsaturated methyl esters of tropical and vegetable oils into their saturated counterpart product namely methyl stearate (MS) are industrially interesting conversions for the production of surfactants, emulsifiers, cosmetics, emollients, solid soaps, lubricants and plasticizers [11–14]. Furthermore, hydrogenation reactions of FAMEs to MS are useful model reactions for studying the full hydrogenation reaction of edible oils into saturated triglycerides which are further subjected to interesterification reactions with liquid vegetable oils to yield shortenings, margarines and other foodstuffs containing zero amounts of *trans*-fats [13–33]. In the early 1990s, it was reported that there is a direct association between consumption of *trans*-fats and cardiovascular disease because of the higher concentrations of LDL-cholesterol in the plasma [34–52]. Due to these reports new regulations have been introduced worldwide in order to restrict *trans*-fats consumption which resulted to a demand for food products containing zero amounts of *trans*-fats [34–52]. Since 1911, the industrial partial hydrogenation process of edible oils makes use of heterogeneous nickel catalysts producing high amounts (up to 50%) of undesired *trans*-fats due to *cis*/*trans* geometric isomerization reactions [15–20, 53, 54]. Nowadays, the edible oils hydrogenation industry prefers the route of full hydrogenation of oils to hard fats with subsequent interesterification with liquid vegetable oils to avoid the formation of *trans*-fats [21–33, 40, 41, 43, 47, 55]. Thus, there is a need for the development of a novel highly selective industrial partial hydrogenation process of edible oils to foodstuffs with a zero content of *trans*-fats.

In 1989, one of us in cooperation with Fell and Bahrmann [56–59] has developed a novel class of ligands i.e. the sulfonated phosphites which are stable systems in hydrolysis side-reactions. Rhodium complexes modified with sulfonated phosphites were used as catalysts in hydroformylation reactions of olefins under mild reaction conditions in organic solvents and exhibited higher selectivities towards the desired linear aldehydes compared to rhodium complexes modified with conventional triphenylphosphite or triphenylphosphine ligands under the same reaction conditions [56–59]. Such monodentate sulfonated phosphite ligands have been also used by Favre et al. [60] to modify rhodium catalysts for the hydroformylation of olefins in ionic liquids/organic two-phase systems and the Rh/monodentate sulfonated phosphite catalyst could be easily separated in the ionic liquid phase containing the catalyst from the organic phase containing the products by a simple phase separation. Recycling experiments proved that the high n/iso-ratios of the aldehydes obtained with Rh/monodentate sulfonated phosphite catalysts remained high in two consecutive runs and that the n/iso-ratios of aldehydes with Rh/monodentate sulfonated phosphite catalysts were also higher compared to their corresponding rhodium catalysts modified with conventional phosphine ligands [60].

Recently, we reported [14] the hydrogenation of methyl esters of palm kernel and sunflower oils to the saturated methyl stearate catalyzed by rhodium and ruthenium complexes of monodentate sulfonated triphenylphosphite ligands in the absence or presence of organic solvents. We now report an expansion of our work on the use of sulfonated phosphites with the development of the novel full hydrogenation reaction of C=C units of renewable polyunsaturated methyl esters of palm kernel and sunflower oils into their saturated counterpart methyl stearate (MS) catalyzed by highly active rhodium, ruthenium and nickel complexes with bidentate hexasulfonated *o*-phenylendiphosphite ligands under mild reaction conditions in homogeneous systems [13]. The full hydrogenation of polyunsaturated methyl esters of palm kernel and sunflower oils into MS are useful model reactions for studying the full hydrogenation reaction of edible oils into saturated triglycerides which are further subjected to interesterification reactions with liquid vegetable oils to yield foodstuffs containing zero amounts of *trans*-fats. MS could be also used as starting material for industrial catalytic hydrogenolysis processes into stearyl alcohol which is an important industrial fatty alcohol and is further proceeded for the manufacture of surfactants, emulsifiers, cosmetics, emollients, solid soaps, lubricants and plasticizers. The bulkiness of the transition metal bidentate hexasulfonated

o-phenylendiphosphite anionic catalytic system bearing large triisooctylammonium counter cations could offer the possibility of the easy separation of the catalysts from the reaction mixtures by means of a membrane [13]. To our knowledge, this is the first example of a hydrogenation reaction catalyzed by transition metals modified with a chelating sulfonated phosphite.

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. $RhCl_3 \cdot 3H_2O$ was purchased from Acros Organics, $RuCl_3 \cdot 3H_2O$ and $NiCl_2 \cdot 6H_2O$ were obtained from Alfa Aesar and all three were used as received. 3,5-pyrocatecholdisulfonic acid disodium salt monohydrate (1,2-Dihydroxybenzene-3,5-disulfonic acid disodium salt monohydrate, Tiron monohydrate) was purchased from Alfa Aesar. Triisooctylamine and triphenylphosphite were purchased from Sigma-Aldrich. Sulfuric acid was purchased from Fluka. 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). 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 (MEPKO, Edenor® ME PK 12–18 F) and methyl esters of sunflower oil (MESO, Sunflower Fatty Acid ME®) were supplied by Cognis GmbH (today BASF) and used without any further purification. Aluminium oxide 90 active neutral (70–230 mesh) was purchased from Merck. Sunflower oil from *Helianthus annuus* was purchased from Fluka. Methyl heptadecanoate was purchased from Fluka.

2.2 Synthesis of the Hydrolysis Stable Bidentate Hexasulfonated *o*-Phenylendiphosphite Triisooctylammonium Salt (HSPDP) Ligand

The pathway for the synthesis of hexasulfonated o-phenylendiphosphite triisooctylammonium salt (HSPDP) ligand is shown in Fig. 1. Addition of 2 M aqueous H_2SO_4 to 3,5-pyrocatecholdisulfonic acid disodium salt monohydrate (1,2-Dihydroxybenzene-3,5-disulfonic acid disodium salt monohydrate, Tiron monohydrate) aqueous solution yields 3,5-pyrocatecholdisulfonic acid. Reaction of 3,5-pyrocatecholdisulfonic acid in water with triisooctylamine (TiOA) in toluene in an aqueous/organic two-phase system forms 3,5-pyrocatecholdisulfonic acid triisooctylammonium salt in the organic toluene phase. Subsequent separation of the upper organic phase, drying and transesterification of 3,5-pyrocatecholdisulfonic acid triisooctylammonium salt with triphenylphosphite gives (after removal of phenol by distillation) the HSPDP ligand with a yield of 66.0 mol%.

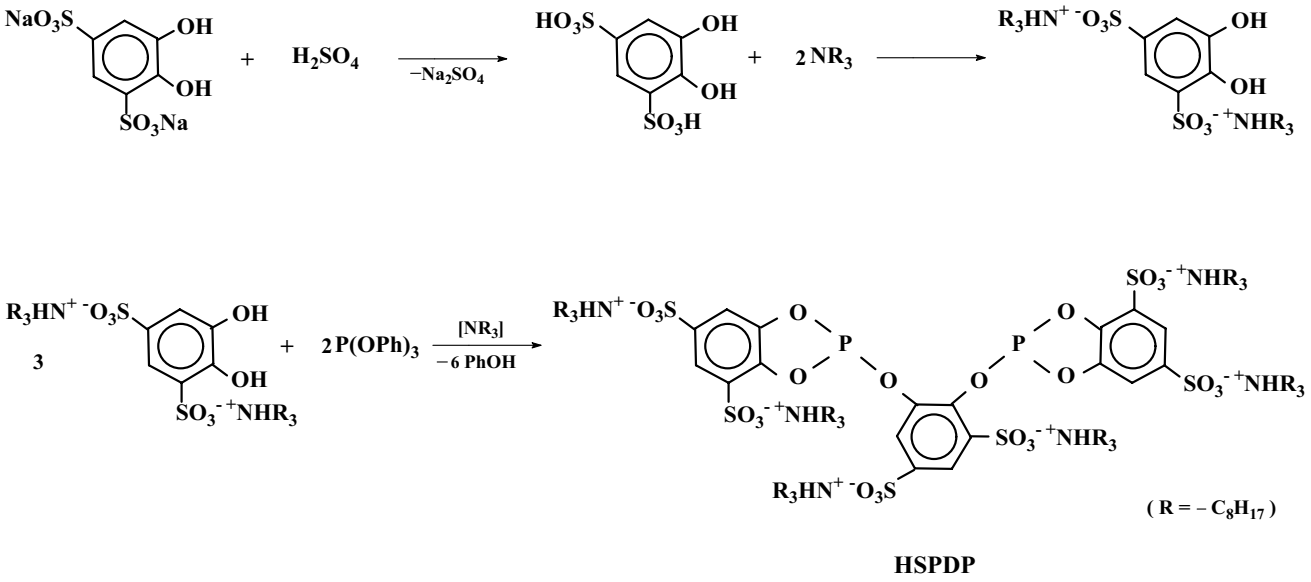

Fig. 1 Synthesis of the hexasulfonated *o*-phenylendiphosphite triisooctylammonium salt (HSPDP) ligand

2.2.1 Preparation Procedure for the HSPDP Ligand

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 332.23 g (1.0 mol) 3,5-pyrocatecholdisulfonic acid disodium salt monohydrate (1,2-Dihydroxybenzene-3,5-disulfonic acid disodium salt monohydrate) which was dissolved under stirring in 600 ml of deoxygenated demineralized water. Through the dropping funnel were added 400 ml of a 2M aqueous H_2SO_4 solution to the cooled 1,2-Dihydroxybenzene-3,5-disulfonic acid disodium salt aqueous solution using an ice/water bath in a period of 2 h under intensive stirring. A mixture of 707.36 g (2.0 mol) triisooctylamine (TiOA) in 800 ml of dried toluene was added dropwise through the dropping funnel and stirred intensively overnight at room temperature. After phase separation the aqueous phase was discarded and the upper organic toluene phase containing the 3,5-pyrocatecholdisulfonic triisooctylammonium salt was dried over activated Na_2SO_4 for several hours. After separation of Na_2SO_4 by filtration, the 3,5-pyrocatecholdisulfonic triisooctylammonium salt/toluene organic phase, was heated under reflux in a Dean–Stark apparatus overnight to remove last amounts of water from the organic mixture. A solution of 206.8 g (0.66 mol) triphenylphophite and 10 g (0.028 mol) TiOA in 600 ml dried toluene was added dropwise to the 3,5-pyrocatecholdisulfonic triisooctylammonium salt/toluene mixture under stirring at 150 °C for 3 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 30 °C under 1 torr vacuum within a period of 70 h to give an amount of 124 g of removed phenol. The yield of the transesterification reaction, based on the total amount of removed phenol by distillation, was 66% and any amounts of unreacted triphenylphosphite could not be removed by distillation at higher temperatures up to 70 °C under 0.01 torr vacuum from the mixture and a yellow, highly viscous liquid remained which was the bidentate hexasulfonated *o*-phenylendiphosphite triisooctylammonium salt (HSPDP) ligand. The HSPDP ligand was analysed by $^{31}P\{^1H\}$NMR (121 MHz, referenced to external 85% H_3PO_4) on a Varian Unity Plus 300/54 spectrometer in $CDCl_3$ at 25 °C. δ: HSPDP = + 130.6 ppm; impurities from triphenylphosphite = + 128.9 ppm.

2.3 Transesterification Reaction of Sunflower Oil with Methanol to Obtain MESO1

A 500-ml, three-necked, round-bottom flask, equipped with a mechanical stirrer, a thermometer and a condenser was charged with 161.0 g of sunflower oil and a solution of 101.0 g methanol containing 1.61 g of NaOH. The mixture was stirred at 55–58 °C for 2 h. The course of the reaction was followed by thin layer chromatography. The reaction mixture was then cooled and further stirred for 1 h at room temperature. After phase separation resulted in the isolation of the methyl esters of sunflower oil (MESO1) and the glycerol. The glycerol phase (bottom layer) was removed and kept in a separate container. The MESO1 phase (top layer) was washed with distilled water several times (pH 5.7), dried over Na_2SO_4 to obtain 110.4 g of MESO1 mixture which was used as starting material in the Ni/HSPDP-catalyzed hydrogenation reaction without further purification. The composition of MESO1 was determined by GC and is given in Table 2.

2.4 Typical Hydrogenation Procedure

The autoclave was thoroughly cleaned and followed by series of treatment of the autoclave at elevated temperature (100 °C) and pressure (40 bar of H_2) within 1 h each time in the presence of HSPDP/methanol and the absence of any transition metals in order to be sure that no memory effects of the autoclave regarding previous transition metal catalytic systems are still operative. The hydrogenation reactions of C=C units of methyl esters of palm kernel and sunflower oils were than performed in the presence of Rh- and Ru-HSPDP complexes in organic solvents and typical hydrogenation reaction conditions were given below. The Rh- or Ru-HSPD catalyst precursor was first synthesized by dissolving the amount of HSPDP ligand in 10 ml of dried organic solvent and complexation with $RhCl_3{\cdot}3H_2O$, $RuCl_3{\cdot}3H_2O$ or $NiCl_2{\cdot}6H_2O$ under argon. The metal/HSPDP catalyst precursor solution was transferred into an *Autoclave Engineers* autoclave of a nominal volume of 100 ml which was previously evacuated and filled with argon together with the amount of methyl ester of palm kernel or sunflower oils. After a number of pressurising-depressurising cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured by H_2 and contents were heated from 70 up to 170 °C with stirring using a stir bar driven by an IKA magnetic stirrer (poorer mixing) with a stirring rate of 750 rpm. At the reaction temperatures the hydrogen pressures were from 10 up to 50 bar. After the reaction the autoclave was cooled to room temperature, depressurized through a vent and the hydrogenation reaction mixture was removed. The samples of the reaction mixtures after filtration over neutral alumina and addition of methyl heptadecanoate as standard were analyzed by gas chromatography (GC) and the obtained results are given in Tables 1 and 2. Emphasis has been placed in all reaction described in Tables 1 and 2 in order to obtain reproducible results.

2.5 Analysis of the Starting Materials Methyl Esters of Palm Kernel and Sunflower Oils and the Products of the Hydrogenation Reaction

During the hydrogenation reaction an amount of the starting material containing *cis*-olefinic bonds undergoes positional and geometric isomerizations reactions to form several different positional and *trans*-isomers especially under the conditions were the selectivity to methyl stearate was below 50 mol%. These various *cis*/*trans*- and positional FAME isomers obtained as products in the mixture after the reaction and also the various FAME compounds in the starting materials of methyl esters of palm kernel and sunflower oils were identified by comparison of GC and GC/MS analytic data with data for authentic samples. GC/MS was measured on a Varian Star 3400CX GC coupled with a Varian Saturn 2000 ion trap MS and equipped with a flame ionization detector (FID) and a SP-2560 capillary column (100 m × 0.25 mm i.d. × 0.2 µm film thickness) which was purchased from Supelco (Athens, Greece). The SP-2560 capillary column is one of the two columns applied in the approved American Oil Chemists' Society (AOCS) official method Ce 1h-05 for the determination of *cis*-, *trans*-, saturated, monounsaturated and polyunsaturated fatty acids in vegetable or non-ruminant animal oils and fats by capillary GLC method [61]. Carrier gas was N_2 at 230 kPa. The oven temperature was initially set at 170 °C for 0 min and then increased to 220 °C with a rate of 1 °C/min. The injector and detector temperatures were set both at 220 °C. GC analyses were performed on a Shimadzu GC-14B equipped with a FID detector and with the SP-2560 capillary column and the conditions were the same as described above in GC/MS analyses.

3 Results and Discussion

3.1 Full Hydrogenation Reactions of Unsaturated Methyl Esters of Palm Kernel Oil (MEPKO) Catalyzed by Rh- and Ru–HSPDP Complexes

The starting material MEPKO applied in the catalytic full hydrogenation reactions contained only 15.2 mol% of C18 FAMEs with the proportion of 1.78 mol% methyl stearate (MS, C18:0), 11.6 mol% methyl oleate [MO, C18:1 (9c)] and 1.82 mol% methyl linoleate [ML, C18:2 (9c,12c)]. The content of C18 FAMEs was than calculated to 100 mol% to give 11.7 mol% of C18:0 ester, 76.3 mol% of C18:1 compound and 12.0 mol% of the C18:2 ester (Table 1). The mixture of MEPKO except the C18 FAMEs further contained the following saturated fatty esters (Table 1): 0.2 mol% methyl caprate (C10:0), 56.4 mol% methyl laurate (C12:0), 19.1 mol% methyl myristate (C14:0) and 9.1 mol% methyl palmitate (C16:0) which were ignored in the calculations to adjust the C=C units/Metal molar ratios in the catalytic full hydrogenation reactions and probably act as a second solvent for the homogeneous catalytic system together with the added organic solvent which was usually methanol. The full hydrogenation of the unsaturated C18 FAMEs part of MEPKO to yield the desired saturated product methyl stearate (MS, C18:0) was studied in the presence of Rh/HSPDP and Ru/HSPDP catalytic complexes and the obtained results are summarized in Table 1. This study deals with the influence of operating reaction parameters such as temperature, molar ratios of C=C units/Metal and HSPDP/Rh, hydrogen pressure, reaction time, addition of different amounts of methanol as a solvent and of various organic solvents at a stirring rate of 750 rpm (Table 1). First, we investigated the influence of reaction temperature on the catalytic activity and selectivity towards MS (Table 1, entries1/1–1/6). The catalytic activities and selectivities in the Rh/HSPDP-catalyzed full hydrogenation of the polyunsaturated C18 esters part of MEPKO towards the desired saturated product MS increase with increasing temperature from 70 °C up to 90 °C to give TOF values from 49 up to 110 per hour and selectivities from 28.0 mol% up to 48.6 mol% of MS at molar ratios of C=C units/Rh = 300 and HSPDP/Rh = 1 and a hydrogen pressure of 40 bar within 60 min of reaction time at a rhodium concentration of 50 ppm using 10 ml of methanol as a solvent (Table 1, entries 1/1–1/3). Raising the reaction temperature higher has a negative effect on both the catalytic activity and selectivity to MS in the hydrogenation of the unsaturated esters part of MEPKO to give at 120 °C only 93 TOFs per hour and 42.9 mol% of MS (Table 1, entry 1/6). This effect that the catalytic activity increases with increasing temperature and above a specific temperature the activity decreases has been observed in several homogeneously catalyzed hydrogenation reactions of FAMEs [62]. These results were rationalized by assuming that above 90 °C the catalytic active Rh-HSPDP key intermediate species are probably destabilized in the MEPKO hydrogenation reaction mixture. This may be caused due to the less polar nature of MEPKO which consists of large amounts (> 80 mol%) of low polarity compounds such as the saturated C10:0-C16:0 FAMEs. The effect of C=C units/Rh molar ratio in the Rh/HSPDP-catalyzed full hydrogenation of MEPKO at 90 °C, 40 bar hydrogen, 60 min of reaction time, a molar ratio of HSPDP/Rh = 1 and with the same amount of 10 ml of added methanol as a solvent is presented in entries 1/7–1/10. A quantitative selectivity towards MS of 100.0 mol% was obtained at a molar ratio of C=C units/Rh = 50 (entry 1/7) whereas at increasing molar ratios of C=C units/Rh from 100 up to 400 the selectivity to MS decreased from 69.7 mol% down to 34.2 mol%, respectively (entries 1/8–1/10). The activity and selectivity to MS in the Rh/HSPDP-catalyzed full hydrogenation of MEPKO is influenced by the amount of HSPDP ligand

Table 1 Full hydrogenation of the unsaturated C18 esters part of methyl esters of palm kernel oil (MEPKO, Edenor® ME PK 12-18 F) into their saturated (C18:0, MS) counterpart catalyzed by $RhCl_3{\cdot}H_2O$ and $RuCl_3{\cdot}H_2O$ modified with the hydrolysis stable bidentate diphosphite ligand HSPDP

Entry	Catalyst precursor	L/M[f] molar ratio	C=C/M molar ratio	T (°C)	P_{H2} (bar)	t (min)	Solvent (ml)	Selectivity					TOF[c]
								C18:2 (mol%)	C18:1 total (mol%)	*cis*-C18:1 (mol%)	*trans*-C18:1 (mol%)	C18:0 (mol%)	
MEPKO[a]	–	–	–	–	–	–	–	12.0[d]	76.3[e]	76.3[e]	–	11.7	–
1/1	$RhCl_3{\cdot}H_2O$/HSPDP	1	300	70	40	60	MeOH (10)	4.5	67.5	52.2	15.3	28.0	49
1/2	$RhCl_3{\cdot}H_2O$/HSPDP	1	300	80	40	60	MeOH (10)	–	59.0	18.7	40.3	41.0	88
1/3	$RhCl_3{\cdot}H_2O$/HSPDP	1	300	90	40	60	MeOH (10)	–	51.4	8.9	42.5	48.6	110
1/4	$RhCl_3{\cdot}H_2O$/HSPDP	1	300	100	40	60	MeOH (10)	–	52.4	9.7	42.7	47.6	108
1/5	$RhCl_3{\cdot}H_2O$/HSPDP	1	300	110	40	60	MeOH (10)	–	55.3	14.9	40.4	44.7	99
1/6	$RhCl_3{\cdot}H_2O$/HSPDP	1	300	120	40	60	MeOH (10)	–	57.1	15.7	41.4	42.9	93
1/7	$RhCl_3{\cdot}H_2O$/HSPDP	1	50	90	40	60	MeOH (10)	–	–	–	–	100	44
1/8	$RhCl_3{\cdot}H_2O$/HSPDP	1	100	90	40	60	MeOH (10)	–	30.3	–	30.3	69.7	58
1/9	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	60	MeOH (10)	0.4	55.1	–	55.1	44.5	65
1/10	$RhCl_3{\cdot}H_2O$/HSPDP	1	400	90	40	60	MeOH (10)		65.8	16.4	49.4	34.2	90
1/11	$RhCl_3{\cdot}H_2O$/HSPDP	2	100	90	40	60	MeOH (10)	–	55.9	13.8	42.1	44.1	32
1/12	$RhCl_3{\cdot}H_2O$/HSPDP	3	100	90	40	60	MeOH (10)		76.5	53.7	22.8	23.5	12
1/13	$RhCl_3{\cdot}H_2O$/HSPDP	1	100	90	50	60	MeOH (10)	–	9.4	–	9.4	90.6	79
1/14	$RhCl_3{\cdot}H_2O$/HSPDP	1	100	90	60	60	MeOH (10)	–	–	–	–	100	88
1/15	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	30	MeOH (10)	–	61.2	23.9	37.3	38.8	108
1/16	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	90	MeOH (10)	–	35.7	–	35.7	64.3	70
1/17	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	60	MeOH (30)	–	38.0	1.6	36.4	62.0	100
1/18	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	60	MeOH (40)	0.4	19.4	1.5	17.9	80.2	137
1/19	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	60	MeOH (50)	–	23.4	1.8	21.6	76.6	130
1/20	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	60	Ether (40)	10.8	75.7	74.1	1.6	13.5	3
1/21	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	60	MeOAc (40)	10.8	75.5	73.4	2.1	13.7	4
1/22	$RuCl_3{\cdot}H_2O$/HSPDP	1	100	70	50	60	MeOH (10)	2.3	68.7	55.0	13.7	29.0	20
1/23	$RuCl_3{\cdot}H_2O$/HSPDP	1	100	80	50	60	MeOH (10)	1.4	63.2	47.8	15.4	35.4	25
1/24	$RuCl_3{\cdot}H_2O$/HSPDP	1	100	90	50	60	MeOH (10)	–	59.6	38.4	21.2	40.4	30
1/25	$RuCl_3{\cdot}H_2O$/HSPDP	1	100	100	50	60	MeOH (10)	2.4	64.7	45.9	18.8	32.9	20
1/26	$RuCl_3{\cdot}H_2O$/HSPDP	1	200	90	50	60	MeOH (10)	8.2	70.0	61.5	8.5	21.8	20

[a]The starting material methyl esters of palm kernel oil (MEPKO, Edenor® ME PK 12–18 F) which is a product of Cognis GmbH (today BASF) except the C18 compounds (15.2 mol %) further contains: 0.2 mol % methyl decanoate (C10:0), 56.4 mol% methyl dodecanoate (C12:0), 19.1 mol% methyl tetradecanoate (C14:0) and 9.1 mol % methyl palmitate (MP, C16:0). The C18 esters total content of 15.2 mol % with the proportion of 1.78 mol% methyl stearate (C18:0), 11.6 mol% methyl oleate (C18:1) and 1.82 mol % methyl linoleate (C18:2) was calculated to 100 mol% to give 11.7 mol % of C18:0 ester, 76.3 mol % of C18:1 compound and 12.0 mol % of C18:2 ester

[b]Reactions conditions: 1.32 mg (0.005 mmol) $RhCl_3{\cdot}H_2O$; 14.92 mg (0.005 mmol) HSPDP (P/Rh molar ratio = 1); 3.093 g (1.5 mmol of C=C units of the unsaturated C18 esters part) of MEPKO (C=C units/Rh molar ratio = 300); entries 1/1–1/6, [Rh] = 50 ppm; entry1/10, [Rh] = 40 ppm; 2.62 mg (0.01 mmol) $RuCl_3{\cdot}H_2O$; [Ru] = 100 ppm; stirring rate = 750 rpm

[c]Defined as mole of hydrogenate C=C units in the C18:2 and C18:1 compounds in the starting material MEPKO mixture and all other regiomers formed during the course of the reaction per mole of metal per hour

[d]Methyl linoleate (ML), C18:2 (9c, 12c)

[e]Methyl oleate (MO),C18:1 (9c)

[f]L/M refers to the ligand/metal molar ratio

Table 2 Full hydrogenation of the polyunsaturated methyl esters of sunflower oil (MESO Sunflower Fatty Acid ME®; MESO1) into their saturated (C18:0, MS) counterpart catalyzed by $RhCl_3{\cdot}H_2O$, $RuCl_3{\cdot}H_2O$ and $NiCl_2{\cdot}6H_2O$ modified with the hydrolysis stable bidentate diphosphite ligand HSPDP

Entry	Catalyst precursor	L/M[g] molar ratio	C=C/M molar ratio	T (°C)	P_{H2} (bar)	t (min)	Solvent (ml)	Selectivity						TOF[c]
								C18:2 (mol%)	C18:1 total (mol%)		*cis*-C18:1 (mol%)	*trans*-C18:1 (mol%)	C18:0 (mol%)	
MESO[a]	–	–	–	–	–	–	–	70.0[d]	25.3[e]	25.3[e]		–	4.7	–
2/1	$RuCl_3{\cdot}H_2O$/HSPDP	1	500	80	50	60	MeOH (10)	30.5	48.7	38.1	10.6		20.8	200
2/2	$RuCl_3{\cdot}H_2O$/HSPDP	1	500	90	50	60	MeOH (10)	22.7	52.3	33.4	18.9		25.0	240
2/3	$RuCl_3{\cdot}H_2O$/HSPDP	1	500	100	50	60	MeOH (10)	17.2	52.6	35.0	17.6		30.2	260
2/4	$RuCl_3{\cdot}H_2O$/HSPDP	1	500	110	50	60	MeOH (10)	9.5	52.5	26.5	26.0		38.0	300
2/5	$RuCl_3{\cdot}H_2O$/HSPDP	1	500	120	50	60	MeOH (10)	8.0	53.4	22.7	30.7		38.6	310
2/6	$RhCl_3{\cdot}H_2O$/HSPDP	1	200	90	40	60	MeOH (10)	–	2.8	–	2.8		97.2	185
2/7	$RhCl_3{\cdot}H_2O$/HSPDP	1	500	90	40	60	MeOH (10)	–	20.5	8.6	11.9		79.5	350
2/8	$RhCl_3{\cdot}H_2O$/HSPDP	1	1000	90	40	60	MeOH (10)	–	24.2	10.9	13.3		75.8	710
2/9	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	90	40	60	MeOH (10)	–	47.0	18.4	28.6		53.0	1400
2/10	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	90	40	5	MeOH (10)	33.8	51.2	38.0	13.2		15.0	8680
2/11	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	90	40	15	MeOH (10)	10.0	65.9	36.8	29.1		24.1	4800
2/12	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	90	40	30	MeOH (10)	–	59.7	23.3	36.4		40.3	2800
2/13	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	90	40	90	MeOH (10)	–	43.8	18.1	25.7		56.2	930
2/14	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	10	30	MeOH (10)	35.6	54.1	38.4	15.7		10.3	1380
2/15	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	20	30	MeOH (10)	5.9	69.5	25.0	44.5		24.6	2560
2/16	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	30	30	MeOH (10)	0.8	70.0	30.5	39.5		29.2	2760
2/17	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	40	30	MeOH (10)	–	53.6	22.1	31.5		46.4	2800
2/18	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	40	30	MeOH (40)	–	22.9	10.5	12.4		77.1	2900
2/19	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	40	30	MeOH (50)	–	–	–	–		100.0	3800
2/20	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	40	30	Ether (40)	68.0	25.3	25.0	0.3		6.7	80
2/21	$RhCl_3{\cdot}H_2O$/HSPDP	1	2000	80	40	30	MeOAc (40)	67.0	27.6	26.6	1.0		5.4	120
MESO1[f]	–	–	–	–	–	–	–	69.8[d]	25.5[e]	25.5[e]	–		4.7	–
2/22	$NiCl_2{\cdot}6H_2O$/HSPDP	1	500	120	50	60	MeOH (10)	59.2	32.7	28.2	4.5		8.1	54
2/23	$NiCl_2{\cdot}6H_2O$/HSPDP	1	200	160	50	60	MeOH (10)	30.0	54.7	32.2	22.5		15.3	80
2/24	$NiCl_2{\cdot}6H_2O$/HSPDP	1	200	170	70	60	MeOH (10)	24.8	55.8	31.9	23.9		19.4	90

[a]The starting material methyl esters of sunflower oil MESO (Sunflower fatty Acid ME®) which is a product of Cognis GmbH except the C18 compounds with a total content of 94.5% further contains 5.5% methyl palmitate (MP C16:0). The C18 esters total content of 94.5% with the proportion of 4.4% methyl stearate (C18:0), 23.9 mol% methyl oleate (C18:1) and 66.2 mol % methyl linoleate (C18:2) was calculated to 100 mol% to give 4.7 mol % of C18:0 ester, 25.3 mol % of C18:1 ester and 70.0 mol % of C18:2 ester

[b]Reactions conditions: 1.32 mg (0.005 mmol) $RhCl_3{\cdot}H_2O$; 14.92 mg (0.005 mmol) HSPDP (P/Rh molar ratio = 1); 2.073 g (10 mmol of C=C units) of MESO (C=C units/Rh molar ratio = 2000); entries 2/9–2/17, [Rh] = 50 ppm; 2.62 mg (0.01 mmol) $RuCl_3{\cdot}H_2O$; [Ru] = 60 ppm; 1.21 mg (0.005 mmol) $NiCl_2{\cdot}6H_2O$; [Ni] = 35 ppm; stirring rate = 750 rpm

[c]Defined as mole of hydrogenate C=C units in the C18:2 and C18:1 compounds in the starting material MESO or MESO1 mixture and all other regiomers formed during the course of the reaction per mole of metal per hour

[d]Methyl linoleate (ML), C18:2 (9c, 12c)

[e]Methyl oleate (MO),C18:1 (9c)

[f]The starting material methyl esters of sunflower oil MESO1 which was obtained by transesterification reaction of sunflower oil with methanol except the C18 compounds with a total content of 94.14% further contains 5.85% methyl palmitate (MP C16:0). The C18 esters total content of 94.14% with the proportion of 4.37% methyl stearate (C18:0), 24.04 mol% methyl oleate (C18:1) and 65.73 mol % methyl linoleate (C18:2) was calculated to 100 mol% to give 4.7 mol % of C18:0 ester, 25.5 mol % of C18:1 ester and 69.8 mol % of C18:2 ester.

[g]L/M refers to the ligand/metal molar ratio

added to rhodium precursor (entries 1/8, 1/11, 1/12). As expected, the highest catalytic activity (TOF = 58 h^{-1}) and therefore higher selectivity to the final product MS (69.7 mol%) were obtained at the low HSPDP/Rh molar ratio of 1 (entry 1/8) whereas at a higher ligand/metal molar ratio the catalytic activity decreases to give at a ratio of HSPDP/Rh = 3 a catalytic activity of 12 TOFs per hour and a selectivity towards MS of 23.5 mol% (entry 1/12). This lower catalytic activity at higher HSPDP/Rh molar ratios could probably be rationalized by assuming that a competition between the free HSPDP ligand and the C=C units of unsaturated FAME for a coordination site on rhodium takes place which may lead to a retardation in the activation of the MEPKO full hydrogenation reaction. The effect of hydrogen pressure on the Rh/HSPDP-catalyzed full hydrogenation of MEPKO at a reaction temperature of 90 °C and a molar ratio of C=C/Rh = 100 within 60 min of reaction time is shown in Table 1, entries 1/8,1/13,1/14. As expected the catalytic activity and therefore the selectivity towards the final product MS increase with increasing pressure of dihydrogen from 40 to 50 and up to 60 bar to yield MS with 69.7 mol%, 90.6 mol% and 100.0 mol%, respectively (entries 1/8, 1/13 and 1/14). At a shorter reaction time of 30 min (entry 1/15) the selectivity to MS was lower (38.8 mol%) compared with the selectivity of 44.5 mol% to MS within 60 min reaction duration (entry 1/9) under the same reaction conditions. The selectivity towards the saturated product MS increased further at longer reaction times to achieve 64.3 mol% of MS within a reaction time of 90 min (entry 1/16). The amount of added methanol as a solvent has a pronounced effect on the catalytic activity and selectivity towards MS in the Rh/HSPDP-catalyzed hydrogenation reaction of MEPKO and is shown in Table 1, entries 1/9 and 1/17–1/19. The catalytic activity increased from TOF = 65 h^{-1} up to TOF = 137 h^{-1} and the selectivity to MS from 44.5 mol% up to 80.2 mol% with increasing amount of added methanol as a solvent from 10 up to 40 ml at a low rhodium concentration of 50 and 15 ppm, respectively, a reaction temperature of 90 °C, 40 bar hydrogen pressure, molar ratios of MEPKO/Rh = 200 and of HSPDP/Rh = 1 within 60 min reaction time in the organic monophasic system (entries 1/9, 1/17, 1/18). The presence of a larger amount of added methanol has a negative effect on both the catalytic activity and selectivity to MS in the hydrogenation of the unsaturated esters part of MEPKO to give with 50 ml of added methanol a catalytic activity of TOF = 130 h^{-1} and a selectivity to MS of 76.6 mol% (entry 1/19). Using as solvents diethyl ether and methyl acetate the catalytic activities were much lower with TOF = 3 h^{-1} and TOF = 4 h^{-1}, respectively (entries 1/20, 1/21) compared with methanol with TOF = 137 h^{-1} (entry 1/18) using 40 ml of added organic solvent under the same reaction conditions. This remarkable rate enhancement achieved with methanol compared to diethyl ether and methyl acetate in the hydrogenation of MEPKO may be explained by invoking interactions between the polar solvent methanol and catalytic active rhodium key intermediates species modified with the hexasulfonated *o*-phenylendiphosphite bidentate ligand in the organic reaction mixture. We assume that methanol probably shifts the equilibrium of chelated catalytic intermediates where both C=C units and esters groups of MEPKO are coordinated towards non-chelated catalytic complexes, occupy the vacant coordination and also hydrogen bonding stabilizes the non-chelated species which obviously facilitates subsequent steps in the catalytic cycle. The Ru/HSPDP-catalyzed full hydrogenation of MEPKO in methanol (entries 1/22–1/26) proceeds with much lower activities compared with the catalytic activities exhibited Rh/HSPDP complexes in methanol (entries 1/1–1/21). The catalytic activities and selectivities in the Ru/HSPDP-catalyzed full hydrogenation of MEPKO towards MS slightly increase with increasing temperature from 70 °C up to 90 °C to give values from 20 up to 30 TOFs per hour and selectivities from 29.0 mol% up to 40.4 mol% of MS at molar ratios of C=C units/Ru = 100 and HSPDP/Ru = 1 and a hydrogen pressure of 50 bar within 60 min of reaction time at a ruthenium concentration of 100 ppm using 10 ml of methanol as a solvent (Table 1, entries 1/22–1/24). Raising the reaction temperature higher has a negative effect on both the catalytic activity and selectivity to MS in the hydrogenation of the unsaturated esters part of MEPKO to give at 100 °C only 20 TOFs per hour and 32.9 mol% of MS (Table 1, entry 1/25). At a higher C=C units/Ru molar ratio of 200 in the Ru/HSPDP-catalyzed full hydrogenation of MEPKO at 90 °C the catalytic activity and selectivity to MS slightly decreased to give 20 TOFs per hour and 21.8 mol% of MS (entry 1/26).

3.2 Full Hydrogenation Reactions of Unsaturated Methyl Esters of Sunflower Oil (MESO, MESO1) Catalyzed by Rh-, Ru- and Ni–HSPDP Complexes

Table 2 shows the catalytic activity and selectivity of Ru/HSPDP, Rh/HSPDP and Ni/HSPDP complexes in the full hydrogenation of unsaturated methyl esters of sunflower oil to yield the desired product MS in organic monophasic systems. The influence of various parameters was investigated on this hydrogenation reaction such as temperature, C=C units/metal molar ratio, reaction time, dihydrogen pressure, addition of different amounts of methanol as a solvent and of various organic solvents (Table 2). We used as starting materials for the hydrogenation reaction two mixtures of unsaturated methyl esters of sunflower oil the first one MESO which is a product of Cognis GmbH (today BASF) and the second one MESO1 which was obtained by transesterification of sunflower oil with methanol. The catalytic activity and selectivity towards MS in the Ru/HSPDP-catalyzed hydrogenation of MESO increases with increasing

temperature from 80 °C up to 120 °C to give TOFs from 200 up to 310 h^{-1} and selectivities to MS from 20.8 up to 38.6 mol%, respectively, at molar ratios of C=C units/Ru = 500 and HSPDP/Ru = 1 and a hydrogen pressure of 50 bar within 60 min of reaction time at a ruthenium concentration of 60 ppm using 10 ml of methanol as a solvent (Table 2, entries 2/1–2/5). The apparent Arrhenius parameter of the activation energy of the Ru/HSPDP-catalyzed full hydrogenation reaction of MESO in methanol was calculated from results obtained from hydrogenation reactions carried out at temperatures 80–120 °C and are summarized in Table 2, entries 2/1–2/5. The apparent activation energy which was calculated with these data (Fig. 2) amounts to 12.75 kJ/mol. The rather low apparent activation energy of 12.75 kJ/mol indicates for the presence of an active ruthenium catalyst modified with the bidentate HSPDP ligand in the polar medium of MESO in methanol and might suggest that the low reaction rates observed in the Ru/HSPDP-catalyzed full hydrogenation of MEPKO (Table 1, entries 1/22–1/26) are probably caused from the less polar nature of MEPKO starting material mixture in methanol compared to MESO in methanol because MEPKO consists of large amounts of 84.8 mol% of less polar components which are the saturated C10:0-C16:0 FAMEs and these compounds act as a less polar solvent in the MEPKO full hydrogenation reaction mixture. We choose Rh/HSPDP catalysts to study further the full hydrogenation of MESO because Rh/HSPDP complexes exhibited much higher catalytic activities and selectivities to MS compared with those obtained with Ru/HSPDP catalysts in the full hydrogenation of MEPKO (Table 1). At the low C=C units/Rh molar ratio of 200 the selectivity to MS was 97.2 mol% in the Rh/HSPDP-catalyzed full hydrogenation of MESO at a reaction temperature of 90 °C under 40 bar dihydrogen pressure within 60 min of reaction time (entry 2/6) and with increasing C=C units/Rh molar ratios the selectivity to MS drops dramatically to give at a molar ratio of C=C units/Rh = 2000 only 53.0 mol% of

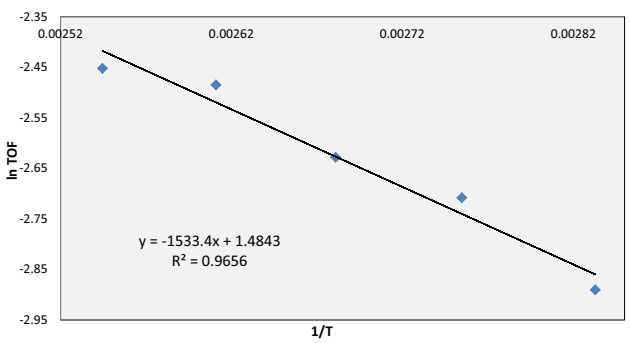

Fig. 2 Calculation of the apparent Arrhenius parameter of the activation energy of the full hydrogenation reaction of MESO catalyzed by Ru/HSPDP complexes in methanol

MS (entry 2/9). However, the catalytic activity at a molar ratio of C=C units/Rh = 200 was only 185 TOFs per hour and with increasing C=C units/Rh molar ratios the catalytic activity considerably increased to reach at a molar ratio of C=C units/Rh = 2000 a value of 1400 TOFs per hour under the same reaction conditions (entries 2/6–2/9). The effect of reaction time in the Rh/HSPDP-catalyzed full hydrogenation of MESO at molar ratios of C=C units/Rh = 2000 and HSPDP/Rh = 1, a reaction temperature of 90 °C under a dihydrogen pressure of 40 bar and a rhodium concentration of 50 ppm using 10 ml of methanol as a solvent is presented in entries 2/9–2/13. At a shorter reaction time of 5 min the catalytic activity of Rh/HSPDP catalysts was as high as 8680 TOFs per hour and the selectivity towards MS of 15.0 mol% under the same reaction conditions (entry 2/10). At longer reaction times the selectivity to MS increased to achieve within 90 min a selectivity of 56.2 mol% of MS and at a lower catalytic activity of TOF = 930 h^{-1} (entry 2/13). The hydrogen pressure has a pronounced effect on both the activity and selectivity to MS in the Rh/HSPDP-catalyzed full hydrogenation of MESO in methanol (Table 2, entries 2/14–2/17). The catalytic activity increased from TOF = 1380 h^{-1} up to TOF = 2800 h^{-1} and the selectivity towards MS from 10.3 mol% up to 46.4 mol% with increasing hydrogen partial pressure from 10 to 40 bar at the low reaction temperature of 80 °C, molar ratios of C=C units/Rh = 2000 and of HSPDP/Rh = 1 and a rhodium concentration of 50 ppm within 30 min reaction time using 10 ml methanol as solvent. However, a relative high formation of undesired *trans*-C18:1 esters of 31.5 mol% was observed with a selectivity to MS of 46.4 mol% at the increased catalytic activity of 2800 TOFs per hour even at the low reaction temperature of 80 °C under 40 bar hydrogen pressure in methanol (entry 2/17). The effect of the amount of added methanol as a solvent in the Rh/HSPDP-catalyzed full hydrogenation reaction of MESO is shown in Table 2, entries 2/17–2/19. Both, the catalytic activity and selectivity to MS increased from TOF = 2800 h^{-1} up to TOF = 3800 h^{-1} and the selectivity to MS from 46.4 mol% up to 100.0 mol% with increasing amount of added methanol as a solvent from 10 up to 50 ml at a low rhodium concentration of 50 and 12 ppm, respectively, a reaction temperature of 80 °C, 40 bar hydrogen pressure, molar ratios of MESO/Rh = 2000 and of HSPDP/Rh = 1 within 30 min reaction time (entries 2/17–2/19). Addition of less polar organic solvents than methanol such as diethyl ether and methyl acetate has a detrimental effect on both the catalytic activity and selectivity towards MS in the Rh/HSPDP catalysed full hydrogenation of MESO. Thus, in the presence of diethyl ether only 80 TOFs per hour with 6.7 mol% of MS (entry 2/20) and with addition of methyl acetate 120 TOFs per hour with 5.4 mol% of MS (entry 2/21) were obtained in the full hydrogenation of MESO compared with 2900 TOFs per hour with

77.1 mol% of MS in the presence of methanol (entry 2/18) under the same reaction conditions. We further applied the less expensive nickel catalyst modified with HSPDP ligands in the hydrogenation reaction of MESO1 using methanol as a solvent (Table 2, entries 2/22–2/24). The Ni/HSPDP-catalyzed full hydrogenation of MESO1 proceeds in general with much lower catalytic activities and selectivities towards MS (entries 2/22–2/24) even under more forcing conditions due to the 3d transition metal nature of nickel compared with the activities exhibited both Ru/HSPDP and Rh/HSPDP catalysts in methanol (entries 2/1–2/21). In the Ni/HSPDP-catalyzed full hydrogenation of MESO1 at molar ratios of HSPDP/Ni = 1 and C=C units/Ni = 500, a reaction temperature of 120 °C under 50 bar dihydrogen pressure and a nickel concentration of 35 ppm using 10 ml of methanol as a solvent within 60 min of reaction time the catalytic activity was low namely 54 TOFs per hour with a selectivity to MS of 8.1 mol% (entry 2/22) whereas Ru/HSPDP catalysts exhibited a higher catalytic activity of 310 TOFs per hour and a higher selectivity to MS of 38.6 mol% under the same reaction conditions (entry 2/5). At a higher temperature of 160 °C and a lower molar ratio of C=C/Ni = 200 the Ni/HSPDP catalytic system exhibited a higher activity of TOF = 80 h^{-1} with a higher selectivity to MS of 15.3 mol % (entry 2/23). Using Ni/HSPDP catalysts under forcing conditions for a homogeneously catalyzed hydrogenation reaction namely a temperature of 170 °C and 70 bar of hydrogen pressure the catalytic activity slightly increases to obtain 90 TOFs per hour with a selectivity to MS of 19.4 mol% (entry 2/24).

4 Conclusions

We have disclosed here a novel study on the full hydrogenation reaction of polyunsaturated methyl esters of palm kernel and sunflower oils into the saturated methyl stearate (MS) employing rhodium, ruthenium and nickel catalysts modified with hexasulfonated *o*-phenylendiphosphite triisooctylammonium salt (HSPDP) ligand using methanol as a solvent. The catalytic hydrogenation of methyl esters of sunflower oil (MESO) proceeds smoothly with Rh/HSPDP complexes to achieve a high catalytic activity of TOF = 8680 h^{-1} at a low reaction temperature of 90 °C under 40 bar of dihydrogen pressure and molar ratios of C=C units/Rh = 2000 and HSPDP/Rh = 1 at a low rhodium concentration of 50 ppm within 5 min of reaction time in 10 ml of methanol. At a higher amount of 50 ml of added methanol the Rh/HSPDP-catalyzed full hydrogenation of MESO yields quantitatively MS at a relative high catalytic activity of 3800 TOFs per hour even at a lower reaction temperature of 80 °C within 30 min of reaction time. Using less expensive Ni/HSPDP catalysts under forcing conditions (T = 170 °C, P_{H2} = 70 bar) low catalytic activities (TOF = 90 h^{-1}) and selectivities towards MS (19.4 mol%) were obtained in methanol. The apparent activation energy of Ru/HSPDP catalyst in the MESO full hydrogenation reaction was calculated and amounts to a low value of 12.75 kJ/mol indicating for the presence of an active ruthenium catalyst modified with the bidentate HSPDP ligand in the polar medium of MESO in methanol. A quantitative selectivity to MS was obtained with, however, much lower catalytic activities of 88 TOFs per hour in the full hydrogenation reaction of methyl esters of palm kernel oil (MEPKO) using Rh/HSPDP catalysts at 90 °C under 60 bar of dihydrogen pressure and molar ratios of C=C units/Rh = 100 and HSPDP/Rh = 1 at a low rhodium concentration of 50 ppm within 60 min of reaction time in 10 ml of methanol. In the hydrogenation reaction of MEPKO at a higher amount of 40 ml of added methanol Rh/HSPDP complexes exhibited a catalytic activity of TOF = 137 h^{-1} and the selectivity to MS was 80.2 mol%. The catalytic activities exhibited Ru/HSPDP complexes in the hydrogenation reaction of MEPKO in methanol were, in general, lower than those achieved by Rh/HSPDP catalysts and have not exceeded the range of 30 TOFs per hour with a selectivity of 40.4 mol% of MS.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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Affiliations

Niki Kaika[1] · Christina Panopoulou[1] · Eleni Anagnostopoulou[1] · Christos Fakas[1] · Panagiotis Lilas[1] · Dimitra Stavroulaki[1] · Georgios Papadogianakis[1]

✉ Georgios Papadogianakis
papadogianakis@chem.uoa.gr

[1] Industrial Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis-Zografou, 157 71 Athens, Greece